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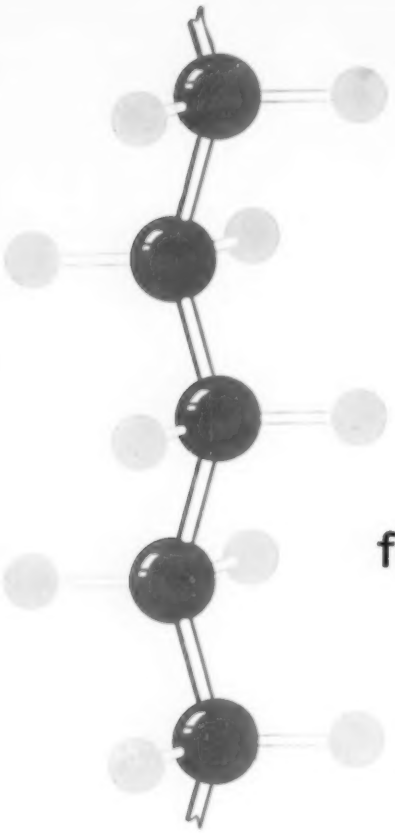
MAY, 1959 • VOLUME 15, NUMBER 5



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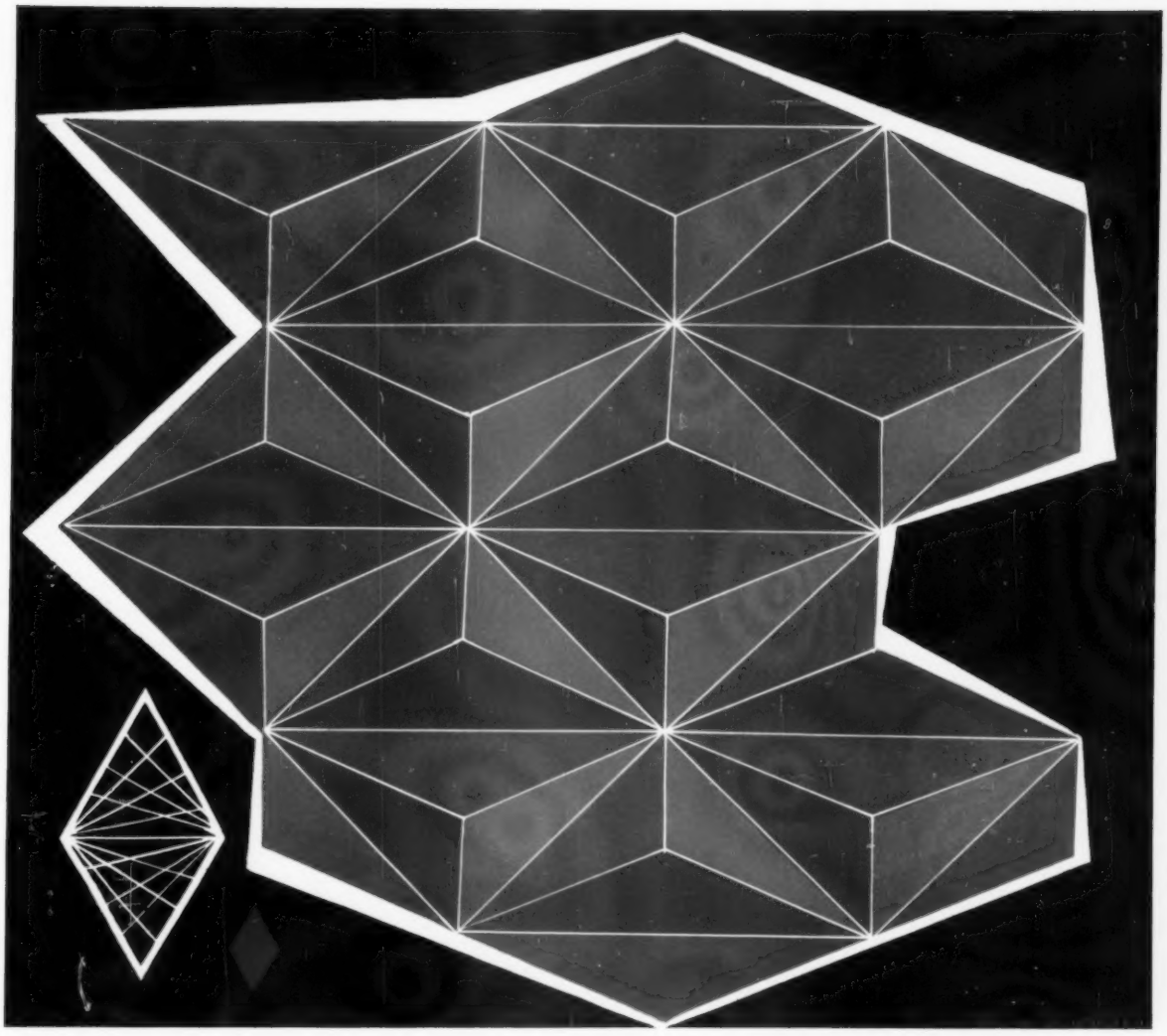

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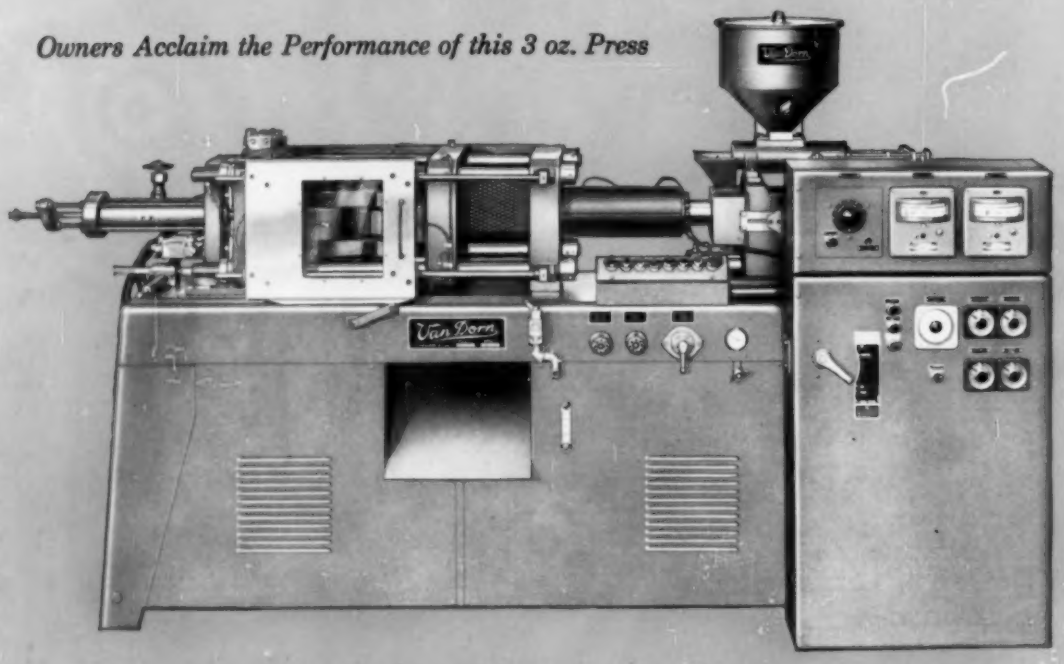

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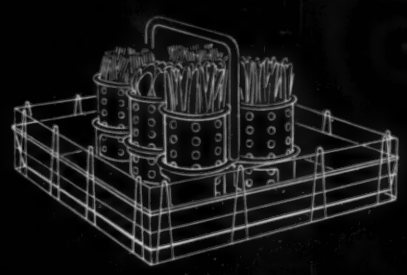

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Brittleness Temp.	D-764-52T	°F.	—200	—180	—160	—100
Impact Strength, izod (⅛" x ½" injection-molded bars)	D-256-54T	ft. lb./in. notch	23	18	13	3
Tensile Strength, Max., 0.2 in./min.	D-638-52T	psi.	3700	3600	3500	3300
Elongation, First Tensile Yield Point	D-638-52T	%	25	25	25	25

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Stiffness	D-747-50	psi.	150,000
Water Absorption (⅛" specimen, 24 hr. immersion @ room temp.)	D-570-54T	%, wgt. gain	<0.01
Flammability	D-635-44	in./min.	1.0
*Mold Shrinkage, length		in./in.	0.03 to 0.05
width		in./in.	0.02 to 0.04

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VOL. 15, NO. 5, MAY 1959

INDEX

Technical Papers—"Best of ANTEC"

On the Relationship of Physical Properties to Structure in Linear Polymers of Ethylene and Propylene—Laurits T. Muus, N. Gerard McCrum, and Frank C. McGrew 368

Progress in Five Years of Research in Stereospecific Polymerization—Giulio Natta 373

A Visual Analysis of Flow and Mixing in Extruder Screws—B. H. Maddock 383

Chain Rupture by Shear in Molten Polymer—Herbert A. Pohl and J. Kenneth Lund 390

A Review of Stress-Cracking in Polyethylene—John B. Howard 397

Chemistry and Performance of Cyanoacrylate Adhesives—H. W. Coover, Jr., F. B. Joyner, N. H. Shearer, Jr., and T. H. Wicker, Jr. 413

A Comparison of Short-Time Versus Long-Time Properties of Plastic Pipe Under Hydrostatic Pressure—Leonard F. Sansone, Jr. 418

Features

Molding Cycles

Answers to Your Molding Problems 429

Speaking of Extrusion

Effect of Wear on the Delivery Capacity of Extruder Screws—B. H. Maddock 433

National Action

The Best of Antec—How and Why They Were Selected—Eugene C. Quear 367

Membership Barometer—James R. Lampman 367

Regional Technical Conference

Plastics in the Automotive Industry—Detroit Section 443

Departments

Editor's Notebook 275
Technical Meetings Calendar 430
About Members 436
Section News 439
Book Reviews 444
Classified Ads 447
Advertisers' Index 448

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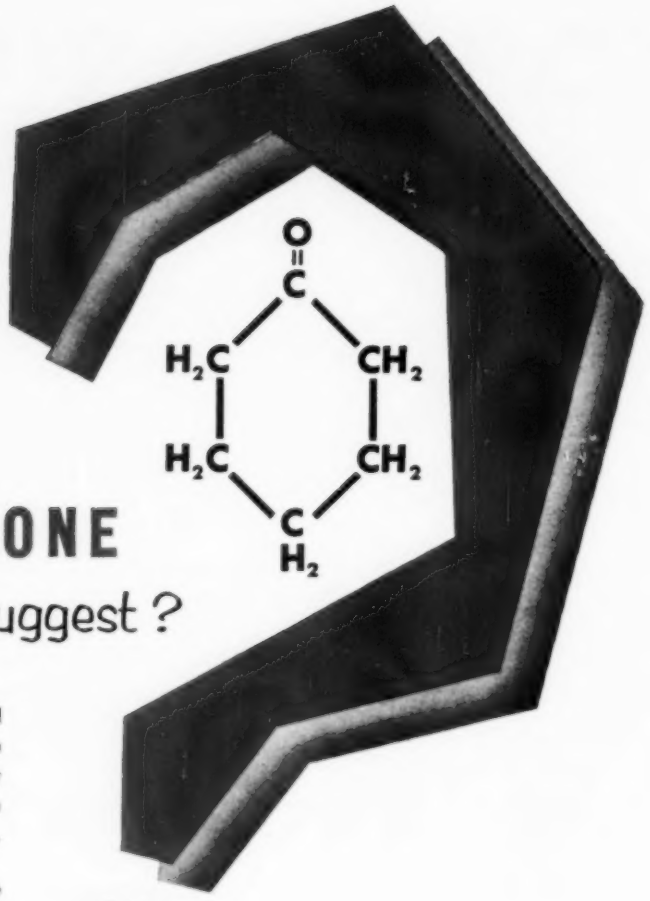

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Charles E. Rhine
Editor

EDITOR'S NOTEBOOK

Next Month—a new feature on moldmaking

The June issue of the *SPE Journal* will inaugurate a new technical feature edited by Ernest J. Csaszar, Newark Die Company. This feature is scheduled for publication bi-monthly and will be designed to keep readers abreast of the latest developments and techniques in moldmaking. Mr. Csaszar is familiar to SPE members as Past President of SPE Newark Section and an eminent authority in the moldmaking field. He will use the moldmaking feature as a "clearing house" for interesting facts and ideas on the design and construction of molds for the plastics industry. He requests that persons having information to submit or questions to ask contact him at the following address: Newark Die Co., Inc., 20 Scott St., Newark 2, N.J.

Have you noticed what happened to Molding Cycles?

Back in January, Louis Paggi changed the format of Molding Cycles feature to a question-and-answer forum on molding problems. A quick run through several issues will reveal some interesting and authoritative answers to questions plaguing molders every day. Lou has had 32 years of plastics experience—all of it is available to you. Just send your questions to Louis Paggi, Sales Service Laboratory, Polychemicals Dept., E.I. du Pont de Nemours & Co., Inc., Wilmington 98, Delaware. If your question is selected for publication in the *SPE Journal*, your name will be withheld from publication.

This may be for you

The SPE National Publications Committee is considering starting a new Journal feature on Plastics in Tooling. If so, we want a top-notch man in this field as editor. The editor for this feature should be one who "gets around" and is able to submit an interesting report on a bi-monthly basis. If you would like to try for this rewarding job, please write me stating your qualifications.

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A series for plastics and packaging executives by the makers of PETROTHENE® polyethylene resins

NOV. 1959 U.S. Industrial Chemicals Co., Division of National Distillers and Chemical Corporation 99 Park Ave., N.Y. 16, N.Y.

Packaging Notes

Easy opening feature for poly packaging is a "DACRON" cord set into the film. The feature is available for any type of polyethylene extrusion lamination, in both roll or pouch form. The cord can be imbedded in the surface of the poly coating, or placed between the poly coating and the material to which the polyethylene is applied. Pouches can also be fabricated with the cord sealed into the side seals of the pouch.

The cord feature is said to be especially suited to packages for cheese, meat, all kinds of dry products, cocoa powders, drink mixes and heat-in-the-pouch items.

Carrots are being marketed in full color, gravure printed poly bags. Appetizing illustrations appear on the face of the bags, along with smaller vignettes and recipes on the back. The bags are said to be the first in the produce field to be printed horizontally.

Universal polyethylene drum is designed to nest inside standard 15 gallon steel or fiber drums. The polyethylene container holds a full 15 gallons and is available with a variety of closures, from standard pipe or buttress threads to external cap closures.

The new drum nests and locks when stacked, needs no pallets. The poly drum is light in weight, unbreakable and carries low freight rates.

A dozen small pockets heat-sealed from a single sheet of polyethylene form a hanging point-of-purchase merchandiser for phonograph needles. The pockets, heat-sealed on three sides, are open at the top for easy removal of the packaged needles. The pocketed polyethylene sheet is stapled to a printed hang card. As the merchandise is sold, the pockets can be restocked. The display is especially suitable for small products that might otherwise be lost or subject to pilferage.

New packaging machine is said to be able to overwrap up to 75 boxes per minute with polyethylene. The machine can also feed, cut and seal a variety of packaging materials. It can handle units three to eight inches wide and a half inch high. Special machine design is necessary for five to nine inch widths. The machine accommodates packages 4¾ to 12½ inches long.

New U.S.I. Polyethylene Plant on Stream: Capacity 75,000,000 lbs. per Year

Plans Already Underway To Double Capacity

A second plant to produce U.S.I. PETROTHENE polyethylene has just gone on stream in Houston, Texas. Capacity of the plant — 75,000,000 pounds per year of low and intermediate density polyethylene resins — increases U.S.I.'s polyethylene production capacity to 175,000,000 pounds per year. The company's other plant, at Tuscola, Ill., now has a 100,000,000-pound-per-year capacity.

New Expansion Will Make U.S.I. 2nd Biggest Producer

When the current expansion program is completed late in 1960, U.S.I. will become the country's second largest producer of polyethylene resins. The new capacity will raise total production of PETROTHENE resins to 250 million pounds.

U.S.I.'s growth in the polyethylene field has been spectacular. Starting with a production capacity of 26 million pounds in 1955, the company will have realized a 900% increase in production when the expanded facilities go on stream.

Along with this growth has gone technical leadership in the field of polyethylene processing, particularly in packaging film. Recently, U.S.I. pioneered a new technique for producing crystal-clear cast poly film that is finding extensive application in large volume overwrap and bread wrap markets. While U.S.I. has specialized in low and medium density resins, it has done extensive research work on a new process for making high density polyethylene. The process is said to be superior to any now in use. U.S.I. also has studied the polypropylenes and other polyolefin copolymers in pilot plant operations.

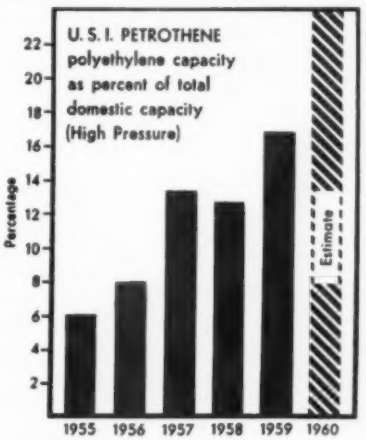


Chart shows spectacular growth of U.S.I. in polyethylene field. Starting as a non-producer less than four years ago, U.S.I. will produce almost one fourth of total U. S. high pressure polyethylene by 1960.

Immediate Expansion planned

Along with the announcement that the plant was in operation, U.S.I. also made public plans to double the capacity of the plant by the end of 1960. This would bring the company's PETROTHENE production in the Houston area to a total of 150,000,000 pounds of polyethylene.

The location of the new plant is especially well suited for improved customer service. The Houston Ship Canal permits shipment by barge. All other means of transportation are readily available. Export shipments will be expedited through use of the extensive port facilities in Houston.

The staff for the Houston plant includes Byron J. Anderson, Plant Manager; Eugene C. Carlson, Technical Superintendent; T. Howard Dantzler, Superintendent of Operations; and E. P. Richards, Chief Engineer.

Wide Range of Resins Available

The new plant, which is already shipping commercial quantities, was rushed to completion some six to eight weeks ahead of schedule when demand for U.S.I. PETROTHENE resins began to outrun supply late in 1958. The plant uses a modification of the conventional high-pressure process already proved in the Tuscola plant. Low density (.915-.924) as well as intermediate density resins (.925-.929) are being produced. These are the polyethylene materials commonly marketed as packaging film, garment bags, squeeze bottles, wire and cable coatings and housewares.

In all, PETROTHENE polyethylenes are available in some 70 different resins, each varying in melt index, density, strength, clarity, gloss, slip, stiffness, and other properties. This wide range of resin properties is a result of U.S.I.'s program of tailor-making resins to meet specific molding and extrusion requirements.

DO YOU HAVE a new polyethylene packaging development you'd like the industry to know about? Make it routine to send your information on new developments to U.S.I. POLYETHYLENE NEWS.

Address the Editor,
U.S.I. POLYETHYLENE NEWS, U. S. Industrial Chemicals Co., Division of National Distillers and Chemical Corp., 99 Park Avenue, New York 16, N.Y.

U.S.I.

Vol. IV, No. 3

POLYETHYLENE PROCESSING TIPS

FACTORS AFFECTING PERMEABILITY OF POLYETHYLENE

Polyethylene is highly impermeable to many liquids and gases. This property is one of the main reasons for polyethylene's widespread use in packaging.

In films and coatings, polyethylene is most often employed as a moisture barrier. It either protects materials from unwanted moisture or prevents loss of irreplaceable moisture from packaged products such as vegetables and meat. At the same time, some degree of permeability to oxygen and carbon dioxide allows leafy vegetables to "breathe."

As a liner for containers and in tubes and bottles, polyethylene's impermeability to numerous organic and inorganic chemicals accounts for its use with countless products – e.g., battery acid, brake fluid, acetone, ethyl alcohol, mustard, catsup, shampoos, detergents, hypochlorite bleach, and adhesives.

Continued development of new packaging applications depends on molders, extruders and manufacturers having a sound understanding of factors affecting the permeability of polyethylene.

Material To Be Packaged

Polyethylene's effectiveness as a barrier depends primarily on the material to be contained. As a broad generalization, the rule of "like permeates like" applies. Hence, polyethylene, a non-polar material, is only very slowly permeated by polar substances. As polarity decreases – and the contained substance more closely resembles polyethylene in structure – permeability increases.

Often not enough is known about the composition of a product to predict permeability behavior. Usually it is advisable to conduct tests, especially for doubtful materials. Cosmetics formulated with essential oils, for example, are frequently troublesome.

The vapor pressure of the contained fluid is important because the amount of a fluid or vapor passing through the barrier increases with its vapor pressure. Both vapor pressure and total gas pressure increase with temperature, so permeability tests of products such as aerosols should be run at the maximum storage temperature likely to be encountered.

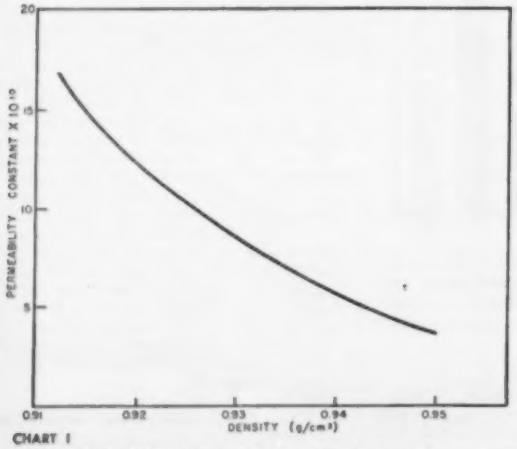


CHART I

Effect of polyethylene density on its permeability to nitrogen.

Effect of Polymer Density

Density is the basic property of polyethylene that affects permeability. As is shown for nitrogen in Chart I, permeability decreases with increase in polymer density. Increased crystallinity of the denser polymer is primarily responsible for this effect.

Effect of Processing Conditions

Permeability is affected adversely by improper processing conditions. Conditions causing non-uniform wall thickness or pinholes in the finished product naturally reduce the effectiveness of the barrier. Oxidation of polyethylene, generally brought about by subjecting it to excessive temperatures over prolonged periods of time, increases its permeability to polar compounds such as water and alcohols.

Pinholes are caused by moisture, resin degradation and air entrapment during fabrication. They can be minimized by keeping the molding powder dry and by holding extrusion temperatures within recommended limits. Often, difficulty with pinholes occurs in forming the parison in bottle blowing. Raising the temperature and increasing back pressure will frequently correct this condition.

Oxidation can be minimized by reducing extrusion temperature and by charging the machine with a special resin prior to shutdown. U.S.I.'s PETROTHENE® 205-1 Shutdown Resin, which withstands exposure at high temperatures, is recommended. Blanketing the hopper and die areas with an inert gas such as nitrogen also reduces oxidation. In blow molding, blowing with nitrogen has the same desirable effect.

Additives may modify polyethylene's permeability. Adding an inert material such as wax may enhance barrier properties provided the added material increases the density and doesn't destroy other essential properties. Other additives, such as aluminum powder, might decrease permeability by increasing the path that molecules of the contained material must traverse through the resin.

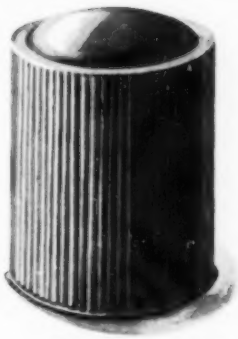
Postforming operations can also be useful. Coating with other polymers such as vinyls or vinylidene chloride offers one means of decreasing permeability. Irradiation, too, generally reduces permeability of all substances through polyethylene.

Technical Assistance from U.S.I.

Each polyethylene packaging application poses special permeability problems requiring a specific solution. The safest approach is to call on U.S.I.'s experienced technical service engineers. They can recommend an appropriate PETROTHENE polyethylene resin for your application and help you establish the best processing conditions.

U.S.I. INDUSTRIAL CHEMICALS CO.
Division of National Distillers and Chemical Corporation
99 Park Avenue, New York 16, N. Y.

HOW ABOUT WOOD FLOUR-FILLED UREA CLOSURES?



Closure Brown

Standard Black

For brown and black closures, PLASKON® Wood Flour-Filled Urea offers high-torque strength, odor-free color-fastness and less dust collection on the shelf—at a price competitive with older general-purpose plastics.

Plaskon

Wood Flour-Filled Urea is now produced in an all-new, automated plant by Allied Chemical. It's a high-quality thermosetting PLASKON Molding Compound. And no molder or user of closures will want to ignore its advantages.

PLASKON Wood Flour-Filled Urea matches the more expensive alpha-cellulose type in all properties, except translucency and range of color. This means you can now have the advantages of urea for all closures—alpha-cellulose for whites and pastels, wood flour-filled for browns and blacks.

Properties of PLASKON Wood Flour-Filled Urea include:

- Superior color-fastness
- Hard, non-electrostatic surfaces (will not attract dust on shelf)
- Greater scratch resistance
- Unaffected by ordinary solvents and highly impermeable to volatile agents

Molders find PLASKON Wood Flour-Filled Urea excellent for high-speed automatic operations. In addition to three years of preproduction research, this low-cost molding compound has been thoroughly tested and proved in commercial manufacturing equipment.

TODAY—take your first step toward investigating this new closure material. Write for technical data and molded samples of PLASKON Wood Flour-Filled Urea.

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Perfectly Practical

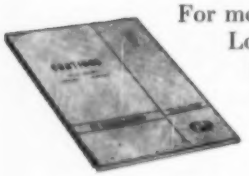
Final inspection is where Logo 222 Series Coatings make production men glow. They provide perfect finishes . . . in a practical way.

The key lies in solids content. Logo 222 Series Coatings contain maximum pigment loading allowable, nearly the same as high-quality enamels. They'll take *much more* thinning. Result: reduced cost *at the gun*, with whites, for example, that give up to 30% greater mileage.

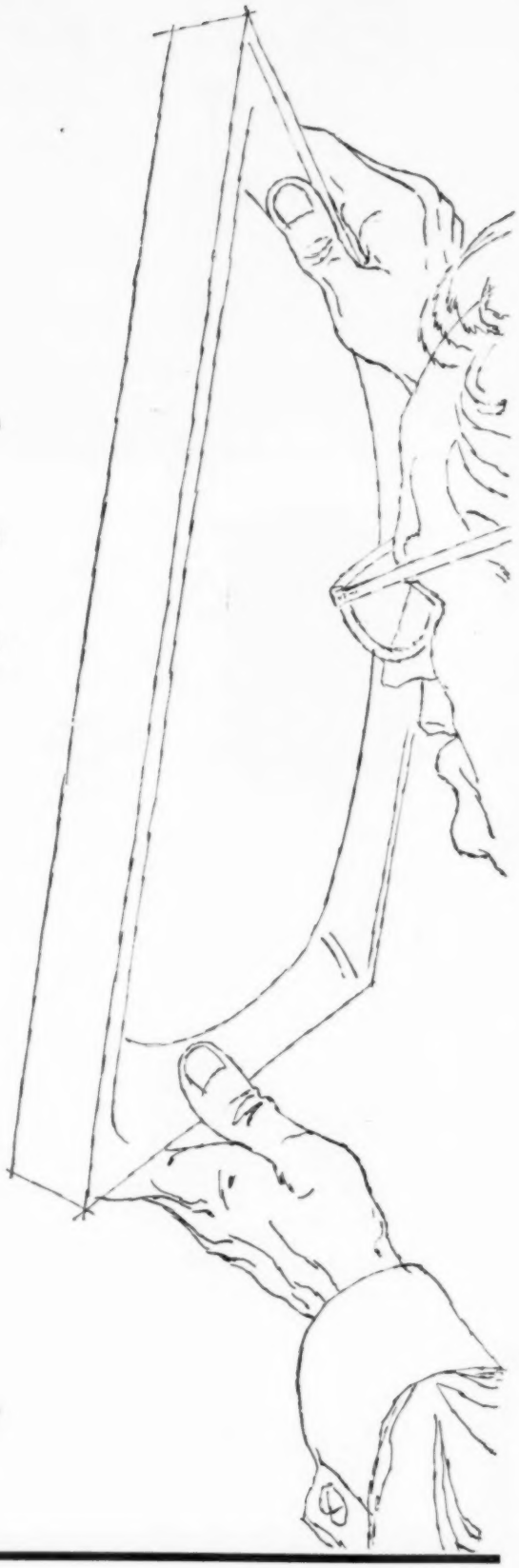
Few coatings *adhere* like Logo 222 Series—especially on corners or sharp edges.

And *fast*—Logo 222 Series Coatings are fast touch dry in 2-4 minutes, pack dry in 20-25 minutes—faster with force drying. Hot stamping may be applied over painted surfaces. Result: conveyorized multiple-color finish lines without rack drying between operations.

Practical? You betcha! Perfect? Let us *show* you in your own plant.



For more information about Logo 222 Series Coatings for thermoplastics, write for Bulletin A-59.



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It's legibility at first sight ...with **BUTYRATE**

There's no mistaking the message of the Edco Tel-A-Flasher sign...and the panels, vacuum formed from sheet of Tenite Butyrate plastic, play a big part in getting that message across—immediately.

Because of Butyrate's brilliant luster, these panels present an eye-catching, eye-pleasing appearance in daytime; and when the sign is internally lighted at night, the sharp contrast of colorful letters with white background gives long-distance legibility.

The low specific heat of Tenite Butyrate makes it an ideal material for sheet thermoforming. With Butyrate there is no need for special preheating oven equipment. Vacuum, air pressure, and mechanical methods are used with inexpensive molds on fast-cycle machines. Available in special weather-resistant formulations and popular sign colors, sheet of Butyrate can also be decorated with lacquers before or after forming.

The outdoor sign industry is but one of many to take advantage of the design and production flexibility of Tenite Butyrate. In addition to its possibilities in sheet forming, this tough thermoplastic material can be rapidly injection molded or continuously extruded to serve a wide range of uses—from steering wheels to skin packaging; from tool handles to telephone housings.

When your product needs call for a material that has superior impact and weather resistance, yet is light in weight, lustrous, easy and economical to form or fabricate —consider Tenite Butyrate. For additional information concerning its physical properties and uses, write to EASTMAN CHEMICAL PRODUCTS, INC., subsidiary of Eastman Kodak Company, KINGSPORT, TENNESSEE.

TENITE
BUTYRATE
an Eastman plastic

EDCO Tel-A-Flasher signs consist of individual letter panels which can be rotated within their frames to any desired angle. Panels are 15"-diameter or 20"-diameter discs of Tenite Butyrate plastic with raised letters (11" or 15" respectively) vacuum formed into their surface. Manufactured and marketed by Electrical Development Company, 719 E. Madison, P. O. Box 3472, Phoenix, Arizona. Butyrate sheet extruded by Jet Specialties Co., Inc., Los Angeles 63, California.

NEW

16-ounce molding machine

Available in 3 new models,

the Farrel Watson-Stillman 16-ounce injection molding machine permits the choice of an injection rate that is ideally suited to the type of plastic to be molded. The three designs differ in injection-ram speeds, but are similar in other respects.

Hydraulically operated, the machine has manual and automatic single-cycle controls.

New bulletin 622-A gives complete details and specifications of this machine. Write for a copy today.

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WS-62

SPECIFICATIONS

	16ES-400	16ES-400M	16ES-400S
Maximum amount of material per shot— Styrene	16	16	16
Injection rate (cubic inches per min.)	1,080	1,310	1,620
Daylight opening	34"	34"	34"
Maximum die sizes	20" x 36" and 21" x 33"		

Which injection rate is right for you?

FARREL WATSON STILLMAN

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The message is:

MONSANTO POLYETHYLENE 14202 NOW WESTERN ELECTRIC APPROVED

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It means passing the most exacting tests in the industry. 14202 Black can meet specifications established to assure an estimated cable service life of 30 years or longer! Western Electric tested for stress crack resistance, low gel content (to minimize localized degradation), appearance, extrusion rates, heat stability. And the testing extended over a long period of time to assure uniformity of properties.
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For complete technical data, write to Monsanto Chemical Company, Plastics Division, Room 1123, Springfield 2, Mass.

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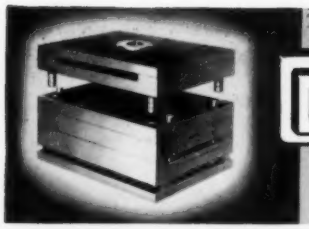

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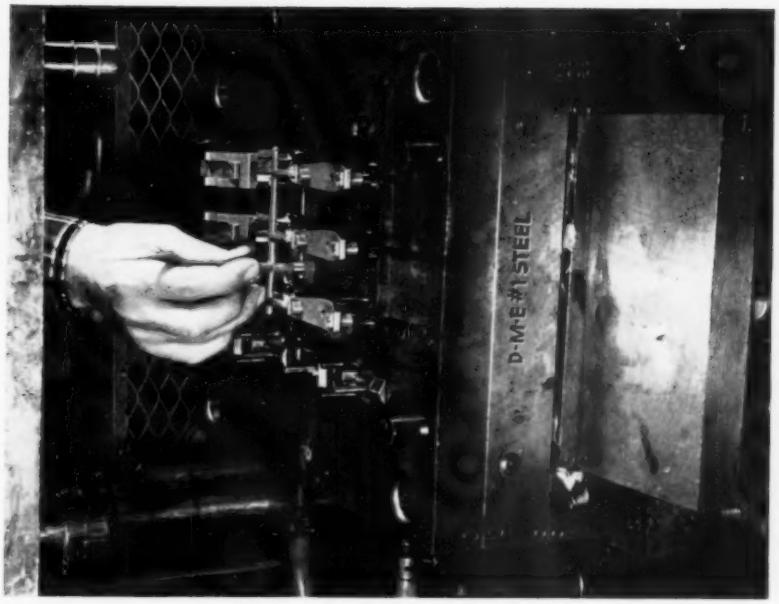

YOU SAVE MORE ON MOLD COSTS WITH OVER 6,000 D-M-E STANDARD MOLD BASES TO CHOOSE FROM

Largest Selection Saves You Time and Money

Whether it's a one-cavity "test" mold or a 60-cavity high production run, chances are D-M-E has the right size Standard Mold Base to fit the job and the molding machine.

D-M-E's 32 standard sizes, up to 23¾" x 35½", with 100 standard cavity plate combinations for each size, give you the largest selection of carbon or alloy steel standards available from any single source.

Save on Design Time, Moldmaking Time, Replacement Parts and Delivery

Design time is reduced by using D-M-E's full-scale Master Layouts and Catalog of specifications and prices. Moldmaking time is reduced because all D-M-E plates are precision ground flat-and-square, ready for cavity layout and machining. Exclusive interchangeability gives you the added saving of immediate replacement of any component part. And D-M-E's seven branch offices and warehouses are always fully stocked with Standard Mold Bases and components to meet your delivery requirements.

Cut Costs on Your Next Program

Start saving on your next moldmaking program, no matter how large or small. Take advantage of D-M-E Quality, Service and Economy.

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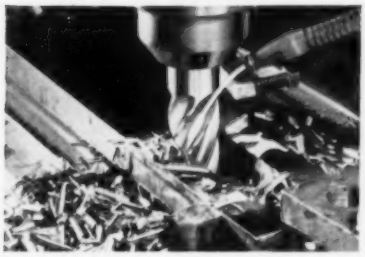

D-M-E's complete stock of moldmakers' tools and supplies can save you time and money! No more waiting for "special" oversize reamers to open up ejector pin holes; no more extra set-up charges. D-M-E has what you need—*in stock*.

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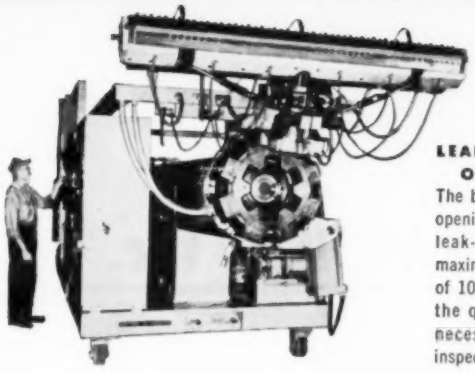

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WESTCHESTER PLASTICS compounds concentrates of color and ready-to-use color blends of conventional and linear polyethylenes and other thermoplastics. When you see WESTCHESTER stamped on your containers of resin, you know that *you are using the custom color that you specified. Write now for detailed information on your thermoplastic color requirements.*

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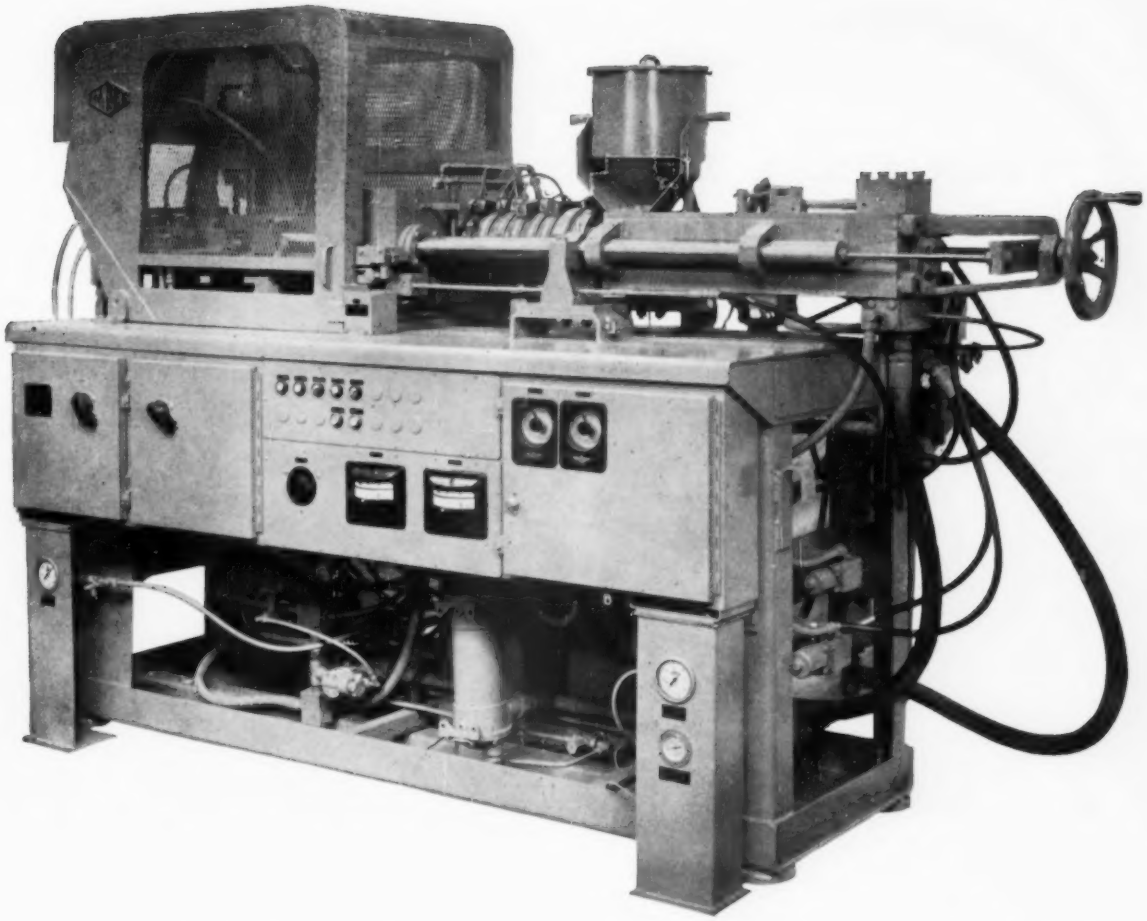

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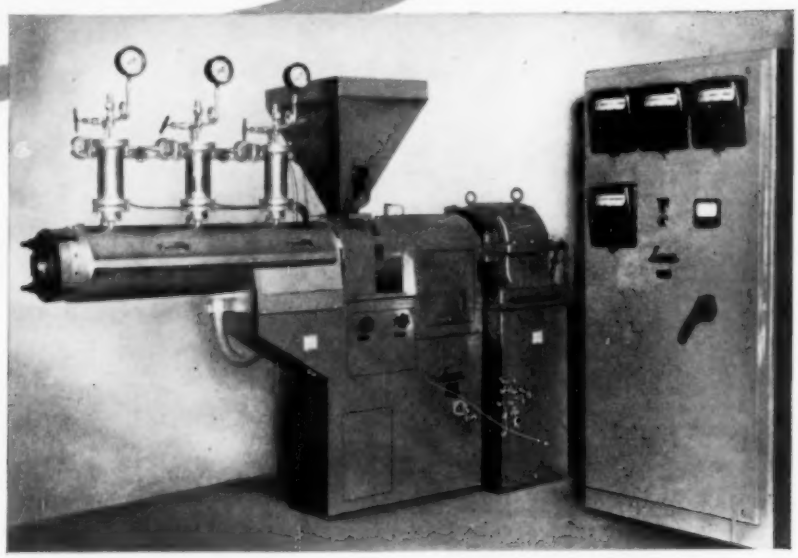

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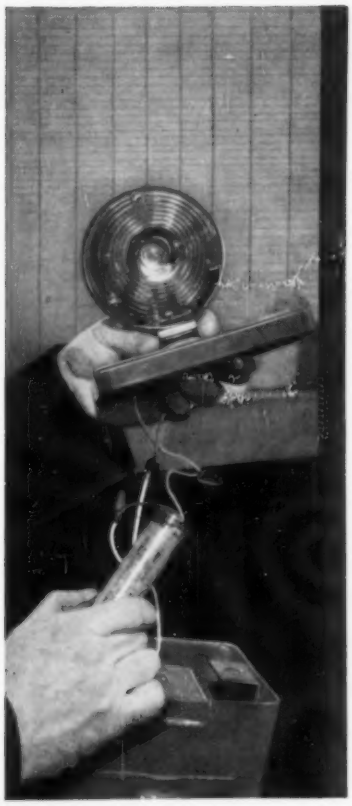

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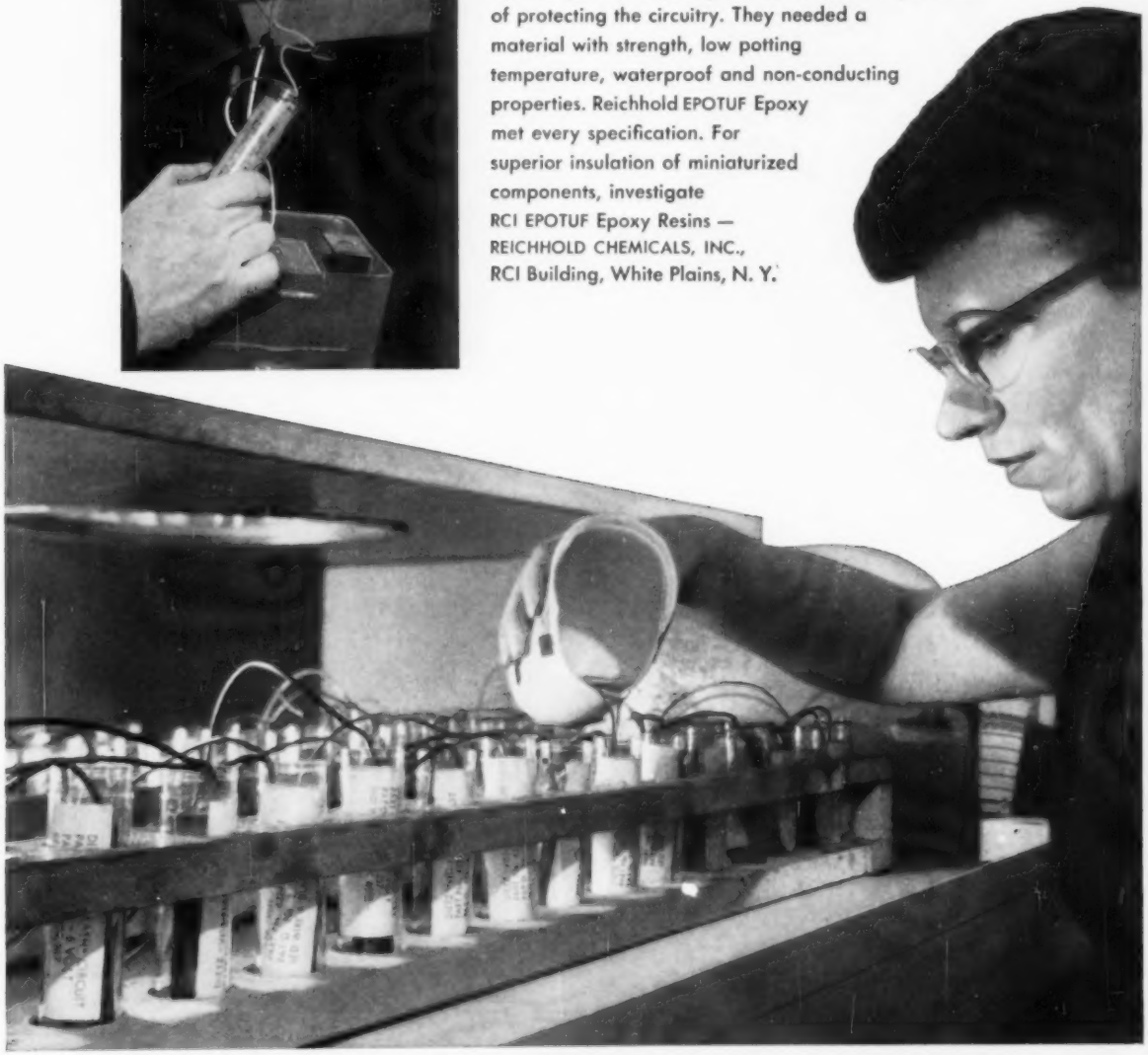
"It has been essential in development of our transistorized warning light"— R. E. Dietz Company, Syracuse, N. Y.

Since 1840 the Dietz Company has lighted America — with everything from kerosene lamps to auto headlights. In developing a new compact warning signal light, the company was faced with the problem of protecting the circuitry. They needed a material with strength, low potting temperature, waterproof and non-conducting properties. Reichhold EPOTUF Epoxy met every specification. For superior insulation of miniaturized components, investigate RCI EPOTUF Epoxy Resins — REICHHOLD CHEMICALS, INC., RCI Building, White Plains, N. Y.



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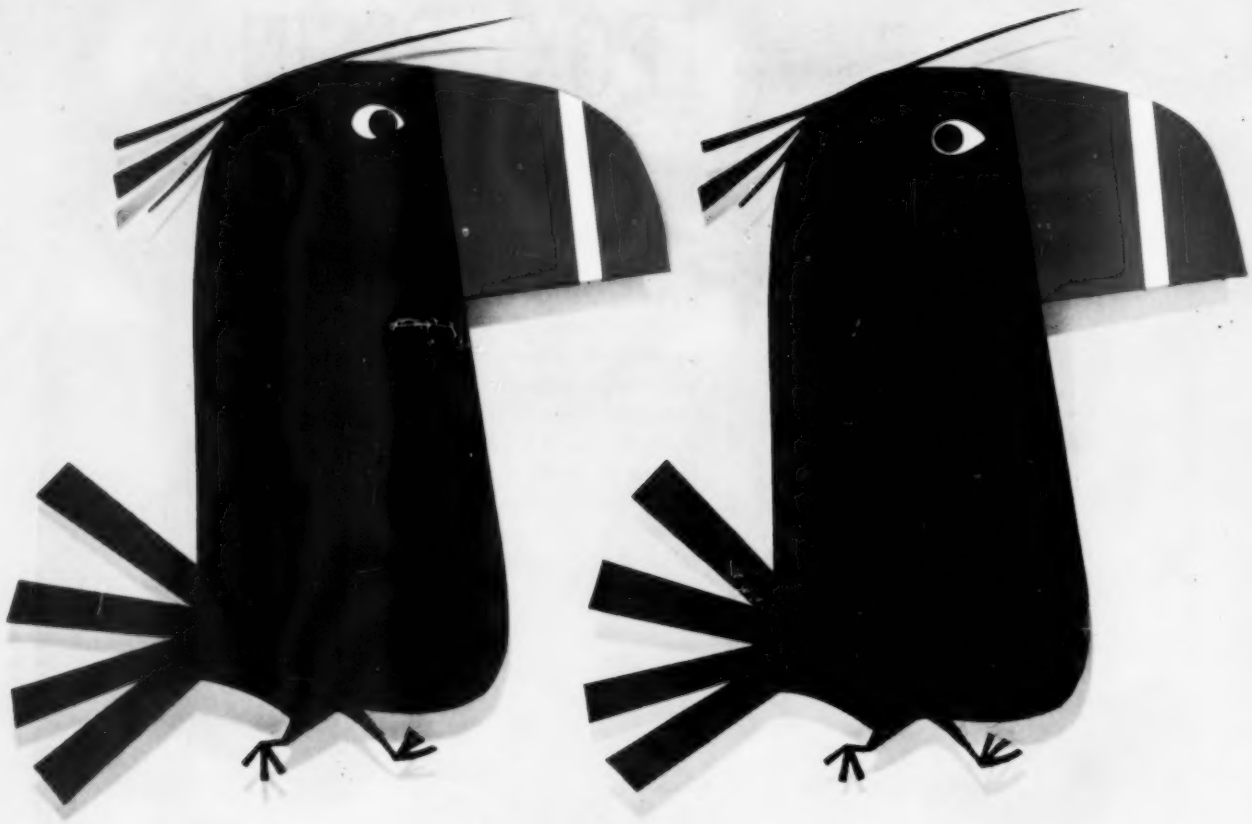

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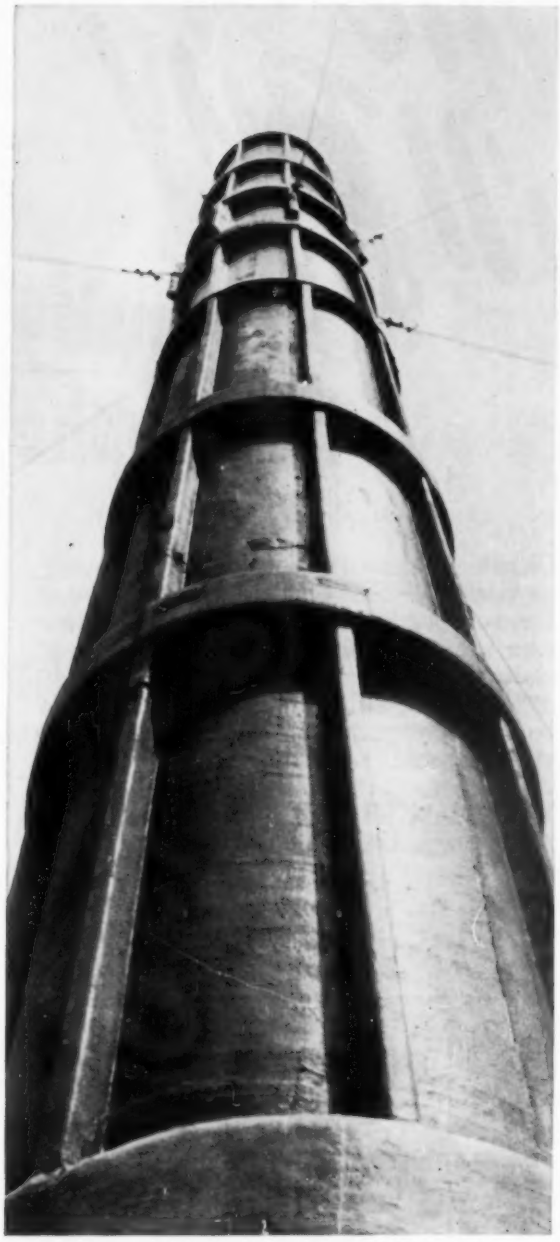

Towering Plastic Smoke Stack—To carry off highly corrosive gases such as hydrochloric acid and ammonium chloride fumes, this 84-foot stack was fabricated entirely of glass-reinforced LAMINAC polyester resin. Made by Canbar Industrial Plastics, Waterloo, Ontario, for a Canadian feed and fertilizer plant, the stack is fabricated in three sections. Total weight of the three plastic sections is only 2,055 pounds. Contrary to conventional materials like metal or brick, the prefabricated plastic reinforced stack was erected quickly and requires little maintenance.

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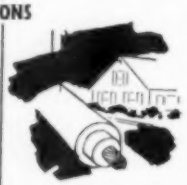

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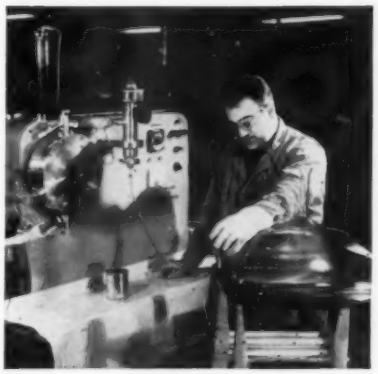
A leading TV tube manufacturer recently presented Dow with a problem involving the laminating of glass panels. They had developed an advanced design for a square-face TV tube which required the laminating of a contoured implosion safety panel directly to the face of the tube. The design would provide greater safety against implosion, produce a brighter picture, eliminate the conventional, dust-catching, separate safety panel and permit the building of slimmer sets. To accomplish this, the manufacturer required a special laminating system and resin material which would meet the following requirements:

1. The method must be adaptable to mass production.
2. The method must provide a stable, adhesive bond to glass.
3. The resulting laminate must be able to withstand rough handling.
4. The resulting laminate must be able to withstand extreme changes in humidity and temperature.
5. Resulting optical properties must be acceptable by E.I.A. color standard for television.



Because no available resin met all these requirements, Dow had to develop a special system which would solve the problem.

Dow's prior extensive research and development work on epoxy resins, coupled with Dow's basic raw material position, had produced new resins whose properties appeared to offer promise of fulfilling the stated requirements. Among these resins were several which were known to: provide high-strength bond to glass; produce stable, heat-and-shock resistant laminate interlayer; exhibit nearly water-white clarity after cure; cure quickly at relatively low temperatures.

Working closely with TV engineers and manufacturers of automatic blending and dispensing equipment, Dow chemists and technical service engineers tailored a unique epoxy system which met every requirement for successful mass production of the new square tube.

Plastiatrics studies, like the one described above, are part of a continuing program by Dow Coatings Technical Service engineers to aid Dow customers in the selection of coatings materials, and in technical matters relating to manufacturing techniques. For more information on Plastiatrics studies, write THE DOW CHEMICAL COMPANY, Midland, Mich., Plastics Sales Dept. 2377EX5.

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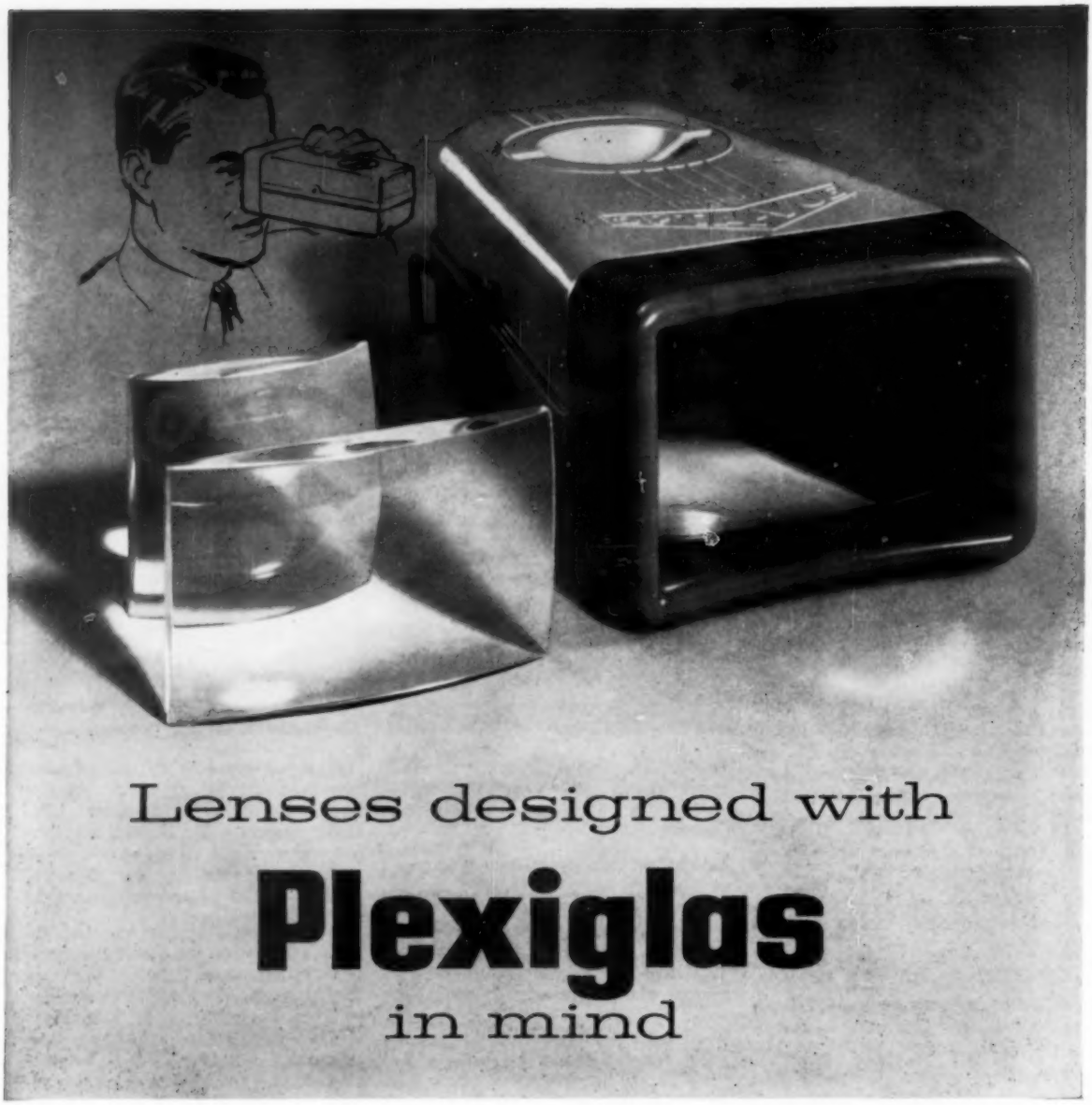

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Edited by Thomas A. Bissell
SPE Executive Secretary

NATIONAL ACTION

The "Best of ANTEC"— How and Why They Were Selected

Eugene C. Quear
Chairman, National Publications Committee

This issue of the SPE Journal features publication of seven papers presented at the Fifteenth SPE Annual Technical Conference in New York City which the SPE Editorial Advisory Board has selected as outstanding contributions to the field of plastics technology. Because of the many excellent papers presented at the 15th ANTEC, it is presumptuous to designate specific papers as being "Best"; however, our Publications Committee feels it desirable to set standards of technical quality to provide a "guiding light" for members of the Society, to give incentive to authors for the improvement of technical papers presented at its meetings, and to reward those who have performed well.

These papers were selected according to rules developed by the SPE Publications Committee. They were chosen on the basis of numerical ratings in which all members of the Editorial Advisory Board participated. The following procedure was employed:

1. All available ANTEC papers were rated by at least two members of the Editorial Advisory Board using the new SPE Journal rating sheet with point score computation.
2. The fifteen papers having the highest point score average were then rated again by at least 10 members of the Board.
3. Of these fifteen, the seven papers having the highest point score average from all Board Members were honored with the designation "Best of ANTEC" and published in this issue.

Other papers that the Editorial Advisory Board feels should be published in the Journal will appear in subsequent issues.

The point score rating sheet used by the Journal provides for a maximum of 100 points on any paper; 30 points maximum for "Value in its field," 30 points maximum for "Value to the profession," 20 points maximum for "Originality," and 20 points maximum for written "Presentation." Each reviewer was requested to rate the papers on each of these points, and the final numerical rating consisted of their total.

This procedure called for more than 500 reviews and ratings during a relatively short period—a monumental task for a 16-man board. For the intensive effort necessary to make this issue possible, I would like to express the deep appreciation of our entire membership to the Retiring-Chairman of the Editorial Advisory Board, Gordon Thayer, Dow Chemical Co.; to Frank W. Reinhart, the newly appointed Board Chairman, National Bureau of Standards, and to the other members of the Board as follows:

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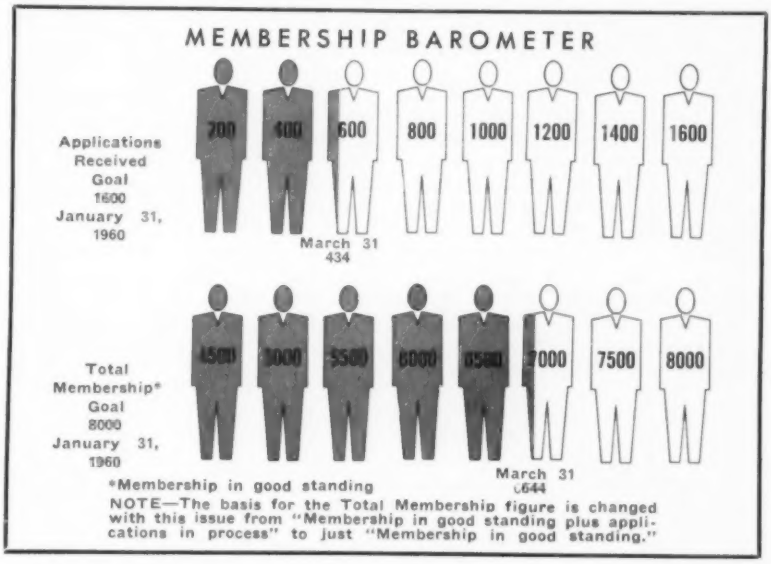

Laurits T. Muus

Laurits T. Muus studied at the Royal Technical University in Copenhagen, receiving the M.Sc. degree in 1942 and the degree of Dr. Techn. in 1955. He was associated with the University until joining DuPont in 1953, where he became a research supervisor in 1958.

N. Gerald McCrum

N. Gerald McCrum completed his B.A. degree at Oxford in 1951. He received the D. Phil. degree in 1954 at the Clarendon Laboratory in Oxford. During 1954-1956, he was an assistant professor in the Dept. of Physics at Pennsylvania State University. He joined DuPont in 1956.

Frank C. McGrew

Frank C. McGrew received a B. Sc. and M.S. degree from the University of Nebraska. In 1937 he received his Ph.D degree from the University of Illinois. He served in many capacities with DuPont and in 1958 became Dir. of Research & Development Div., Polychemicals Dept.

On the Relationship of Physical Properties to Structure in Linear Polymers of Ethylene and Propylene

Laurits T. Muus, N. Gerard McCrum, and Frank C. McGrew
Research & Development Division
Polychemicals Department
E. I. du Pont de Nemours & Company

OF ALL DEMANDS placed on the physical properties of plastics, one of the most important is retention of useful mechanical properties over a wide temperature range. This broad requirement is reflected in many specific ways among which are *toughness* at low temperatures, *stiffness* at intermediate temperatures, and *resistance to creep at* elevated temperatures. Each of these deserves a few words of explanation.

The lower end of the temperature range over which a plastic can be used for a given application is very often set by the temperature at where it becomes shock brittle, that is, the temperature below which it begins to resemble glass in brittleness or loses its impact resistance. No single test is sufficient to determine this minimum use temperature for all applications. Accordingly we employ several, such as Izod, tensile impact, and low-temperature brittleness tests, to rate materials in terms of their ability to resist impact loading. This implies that there is no unique definition of impact resistance or, as we usually say, toughness. On the other hand it is accurate to state that the factors contributing to good impact resistance in a plastic are high strength, low modulus, and high capacity to dissipate mechanical energy. The latter two come into play because a combination of low modulus and extensive conversion of mechanical energy to heat operate to prevent the maximum stress developed in impact loading from exceeding the tensile strength.

Throughout the main part of the useable temperature range of a plastic, a property usually desired is high mechanical modulus, or ability to resist distortion under mechanical stress. A variety of tests are used to measure this property with respect to tension, torsion, and flexure stresses.

In addition to instantaneous deformation under stress, plastics exhibit near room temperature a retarded elastic deformation or primary creep. As a result of this, deformation under constant load increases with time. A convenient way to describe the behavior is to find the decrease of modulus with time. This deformation, however, disappears eventually when the load is removed. In fact, complete recovery is by definition the mark of primary creep.

The creep rate increase flow sets in eventually as use

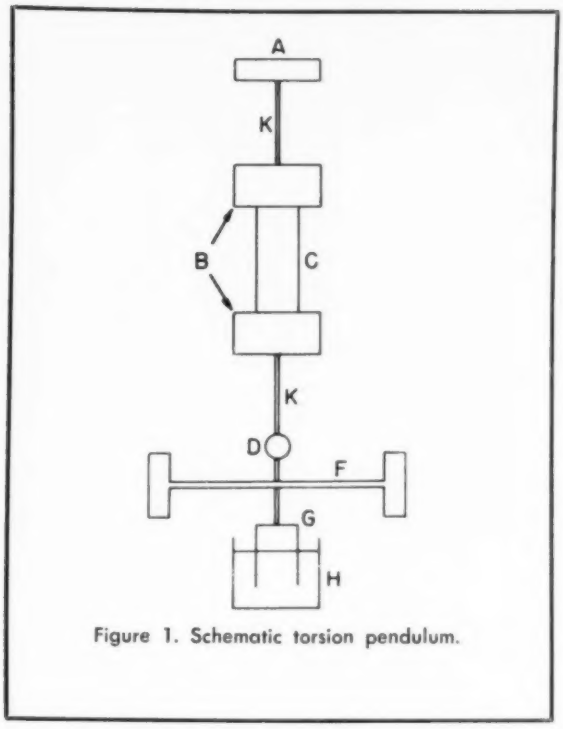

Figure 1. Schematic torsion pendulum.

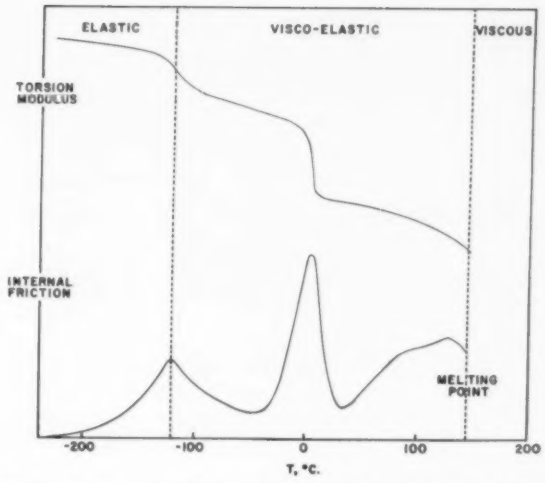

Figure 2. The variation with temperature of the torsion modulus and internal friction for an ideal linear hydrocarbon.

temperature is increased above the range of primary creep. Since flow results in permanent deformation (secondary creep), it often marks the upper limit of usefulness for the plastic. The familiar heat-distortion and Vicat tests, which are used to rank materials in terms of their utility at elevated temperatures, are primarily observations of a pronounced decrease of modulus with time.

Our laboratories have been devoting efforts to this broad question for many years, making use of all the established techniques of polymer investigation and developing new ones of greater usefulness. An experimental method of particular value in relating certain important plastics properties to fundamental molecular characteristics uses of the torsion pendulum to measure both the torsion modulus and the damping capacity of plastics. (Refs. 1, 2, 3, 4).

Fig. 1 shows the operating principle of the torsion pendulum. The measurement is performed in the following manner (Ref. 4): a strip of plastic, C, 60 mils thick, ½" wide, and 2½" long, is clamped to a rigid support at the top. A bar, F, the so-called inertia arm, is clamped to the other end of the strip. Near the ends of the bar, two electromagnets provide a small force to bring the system into torsional oscillation. The torsion modulus is calculated from the frequency of oscillation as well as the weights and dimensions of the system. A small mirror, D, is mounted at the center of the inertia arm. Light reflected from the mirror is focused on a scale. By observing the decrease in amplitude of successive oscillations, the logarithmic decrement can be determined. This quantity is a direct measure of the damping capacity of the specimen.

Straightforward modifications of the instrument allow measurements over a wide temperature range extending even to liquid helium temperatures. The versatility of the method and the significance of the experimental results suggest that it will become an important tool for the plastics engineer as well as for the polymer scientist. In fact, the Deutscher Normenausschuss, which is the German equivalent of ASTM, is now circulating a proposal to use the torsion pendulum in testing plastics.

The data from the torsion pendulum experiments provide information about the temperature dependence of the modulus and the damping capacity. Let us now consider how these properties are related to the performance we can expect of polymers in engineering applications. Specifically, we shall use the data from torsion pendulum experiments to compare the physical properties of polypropylene with those of polyethylene, since these polymers are of keen interest both to plastics engineers and polymer scientists. This is of keen interest with respect to isotactic polypropylene, since this is the variety of polypropylene of most promise to the plastics engineer and for rigid, or as we prefer to call it, higher-density polyethylene, since this is the variety of polyethylene most nearly resembling isotactic polypropylene. Our interest in the comparison, however, stems not only from the similarities between these two types of plastics but from their differences. In their differences lie the criteria the plastics engineer must use in determining the fitness of either to serve in a given application.

The polymer scientist has likewise been attracted to the relationship between these two polymers. Each presents an engrossing problem in polymer structure in its own right. The contrast between the two, moreover, is particularly striking because they differ in molecular structure in such a simple way. Indeed, it appears that polymer scientists' efforts to explain the differences between isotactic polypropylene and higher-density polyethylene may contribute important new knowledge of general significance to the relationship of physical properties of plastics and their molecular structure and configuration.

It is important to note here that the phenomena determining the usefulness of the plastic over the main part of its temperature range, as well as the phenomena that set the lower and upper limits of this range, all involve the *modulus* and the *ability to absorb energy*. It is in this fact that the usefulness of the torsion pendulum lies, because these are exactly the physical properties that are measured. This may be illustrated by

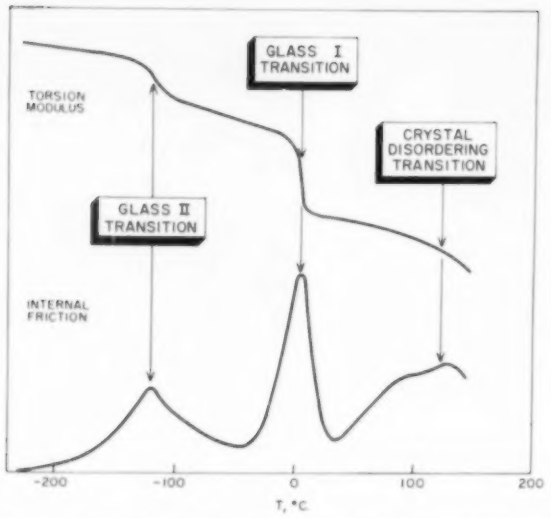

Figure 3. Transitions in the torsion modulus and internal friction for an ideal linear hydrocarbon.

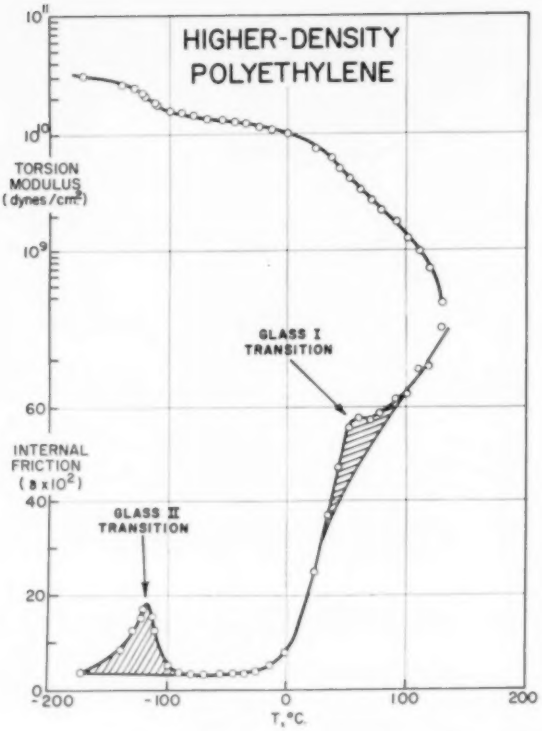

Figure 4. The variation with temperature of the torsion modulus and internal friction for higher-density polyethylene.

reference to the results which would be obtained in a torsion pendulum experiment on an idealized semi-crystalline hydrocarbon polymer (Fig. 2). The upper curve in this figure shows the torsion modulus at a frequency of about one cycle per second as a function of temperature. The lower curve represents the variations with temperature of the damping capacity. This quantity often is called the internal friction, since this term connotes conversion of mechanical energy into heat and thus is one step closer to an interpretation of the physical phenomena in molecular terms.

The chain molecules in the plastic respond to a mechanical stress in a variety of ways. At very low temperatures, where deformation is elastic, the modulus is determined by the forces necessary for stretching and bending chemical bonds. The effect of temperature in this range is merely an increase of intermolecular distances; as the separation of chain molecules increases, there is a small decrease in modulus. Internal friction is very small and the plastic is brittle.

As the temperature is increased the modulus drops rapidly and the internal friction passes through a maximum. Temperature corresponding to a maximum is called a transition temperature. At the transition temperature, deformation is partly elastic, but primary creep or retarded elasticity also takes place. The occurrence of internal friction means in mechanical terms that stress and strain are out of phase. This behavior is usually called viscoelastic and is caused by motions of molecules. In high polymers, such motions usually involve hindered rotation of segments of the chain molecules. When a mechanical stress is applied, part of the energy is converted to heat by these thermal motions. As a consequence the polymer displays mechanical damping. A maximum in damping occurs when the frequency of the torsional oscillation is the same as the frequency of the molecular motions. A large transition produces both a large decrease in modulus and a large increase in damping; both of these tend to increase the impact resistance.

At a still higher temperature but somewhat below the melting point the third type of deformation is observed. This type of deformation reflects viscous flow or secondary creep characteristic of polymeric melts. In this temperature region, the polymer molecules may slip past one another. The polymer has, therefore, a low modulus and is of little practical use.

The various transitions in hydrocarbon polymers are associated with specific molecular motions. Fig. 3 provides the designations which we employ for the transitions that are common to all semi-crystalline hydrocarbon polymers. The "Glass-II" transition occurs in the amorphous regions and is due to hindered rotation of small segments of the polymer chain. Evidence from a variety of polymers suggests that two or three monomer units take part in this motion.

The "Glass-I" transition also occurs in the amorphous regions; it is caused by segmental motions involving approximately 30 monomer units.

Immediately above the "Glass-I" transition there is extensive molecular motion in the amorphous regions. However, the crystallites are still intact. As the temperature is further increased a new transition is encountered. This transition is due primarily to molecular motions in the ordered or crystalline regions. We have designated it as the "Crystal Disordering" transition.

We have felt justified in exhibiting these phenomena in idealized form because these three transitions are common to all semi-crystalline hydrocarbon polymers. However, as we apply the interpretations to actual polymers we must expect that both their magnitudes and their positions on the temperature scale will vary with the molecular structure.

The lower curve in Fig. 4 shows the internal friction curve for a sample of higher-density polyethylene (Ref. 5). The curve has the three peaks characteristic of linear hydrocarbon polymers. The "Glass-II" transition

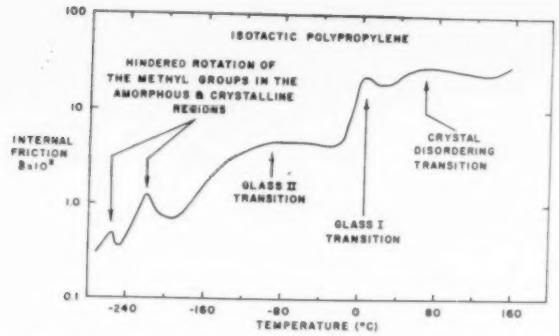

Figure 5. The variation with temperature of the internal friction of isotactic polyproylene.

occurs at about —120°C and is observed as a well resolved peak. The magnitude of the "Glass-I" transition is difficult to determine. It appears at 60°C as a shoulder on the large "Crystalline Disordering" peak.

Fig. 5 shows unpublished data by McCrum (Ref. 5) and Sinnott (Ref. 6) for isotactic polypropylene with high crystallinity. As with higher-density polyethylene, the internal friction curve has peaks corresponding to the "Glass-II," the "Glass-I," and the "Crystalline Disordering" transitions. In addition, the internal friction curve has two peaks below —200°C (Ref. 6). These peaks have no equivalents for higher-density polyethylene, and are so small that they appear only when the logarithm of internal friction is used as ordinate. The small peaks are assigned to hindered rotation of the pendant methyl groups in polypropylene around their threefold symmetry axis. The transition at —260°C takes place in the amorphous regions, and that at —230°C in the crystalline regions.

The lower curve in Fig. 6 shows the same internal friction curve for isotactic polypropylene on a linear scale. The "Glass-II" transition is much smaller than that for higher-density polyethylene. For isotactic polypropylene, the "Glass-II" transition has an origin similar to that in other linear hydrocarbon polymers and is caused by hindered rotation of short chain segments in the amorphous regions.

The "Glass-I" transition, on the other hand, has approximately the same magnitude in these samples of isotactic polypropylene and higher-density polyethylene. Since it is well resolved in isotactic polypropylene, its magnitude can be determined with precision.

The broad "Crystalline Disordering" transition in this polymer is caused by premelting and by disordering within the crystals.

Fig. 7 shows the effect of crystallinity on internal friction and torsion modulus of polypropylene (Ref. 5). High crystallinity is a reflection of high tacticity of the polymer molecules. The magnitude of the "Glass-I" transition at 0°C critically controls the modulus at room temperature. The height of the transition is determined by the amorphous content. For instance, between the temperatures of —260°C and —20°C the modulus of the highly crystalline polypropylene is 30% greater than that of the sample of low crystallinity. However, at 23°C, owing to the intervening transition at 0°C, the difference is more than 500%.

The "Glass-I" and the "Crystal Disordering" transitions overlap in all three samples of polypropylene and occur at approximately the same temperature regardless of the tacticity of the polymer. This implies that the thermal energy necessary to initiate extensive

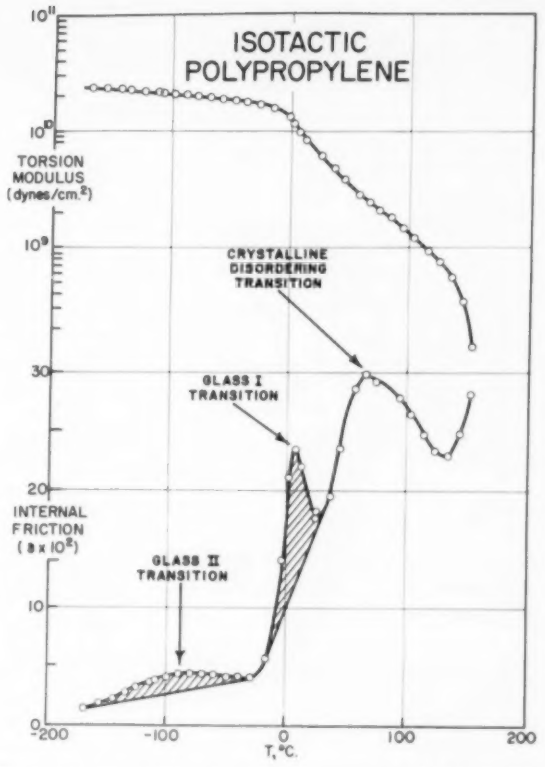

Figure 6. The variation with temperature of the torsion modulus and internal friction for isotactic polyproylene.

molecular motions is essentially independent of sterical configuration.

We are now ready to discuss the influence of the difference in transitional behavior on the torsion modulus of isotactic polypropylene and higher-density polyethylene as shown in Fig. 8. Between —120°C and 0°C the modulus of higher-density polyethylene is considerably smaller than that of isotactic polypropylene. Above 0°C, the torsion moduli are comparable but the relative position of the two curves is reversed for these particular commercial samples of isotactic polypropylene and higher-density polyethylene. The difference is small and well within the range where variations in crystallinity may be decisive for the relative position of the two polymers on the modulus scale. Towards the upper end of the temperature range, isotactic polypropylene has the higher modulus.

The two torsion-modulus curves reflect the fact that the dominant transition for higher-density polyethylene is the sizable "Glass-II" transition at —120°C, whereas the "Glass-I" transition at 60°C has less influence on the torsion modulus curve. The situation is very different for isotactic polypropylene. For this polymer, the "Glass-I" transition at 0°C is dominant and results in a sharp decrease of torsion modulus. On the other hand, the smaller "Glass-II" transition at —100°C makes little impression on the torsion modulus curve.

To go on now to the question of toughness, it is well known that standard tests, such as Izod and tensile-impact tests, show higher-density polyethylene to be tougher than polypropylene. The ASTM brittleness

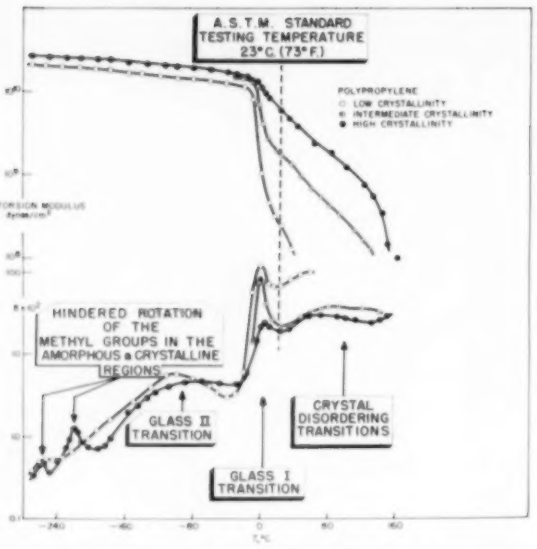

Figure 7. The variation with temperature of the torsion modulus for higher-density polyethylene and for isotactic polypropylene.

temperatures for compression-molded samples of two experimental polymers with comparable melt index are given in Table I. This large disparity in brittleness temperature between higher-density polyethylene and isotactic polypropylene may be understood in terms of the transition behavior of the two materials.

Unfortunately it is not possible to analyze an impact test accurately enough to specify what stress frequency should be used to simulate it. However, it appears that the important frequencies are 1,000 to 10,000 times greater than the frequency of 1 cycle-per-second used in these torsion pendulum experiments. Now it is well known that transitions are displaced toward higher temperatures with increasing frequency. The large "Glass-I" transition in isotactic polypropylene which occurs at 0°C at a frequency of 1 cycle-per-second will be shifted to room temperature or higher at frequencies prevalent in impact tests. This will result in a higher modulus and less energy absorption.

In contrast, the dominant "Glass-II" transition in higher-density polyethylene takes place at such a low temperature that frequency changes cannot cause a displacement of this transition to temperatures near room temperature. Higher-density polyethylene is therefore inherently tougher than isotactic polypropylene in impact experiments at room temperature.

In this discussion, the emphasis has been on the various transitions in polymers of ethylene and propylene. This information has been combined with our knowledge of the molecular structure to present an integrated picture of the molecular motions responsible for the various transitions. It has been demonstrated that difference in transition behavior leads to a brittleness temperature that is much higher for isotactic polypropylene than for higher-density polyethylene, even though the room temperature stiffness is similar for commercial samples of the two polymers. We offer this interpretation of important similarities and differences between these materials in the hope and belief that the work of plastics engineers will be made more effective in the long run by connecting plastics properties to basic structure.

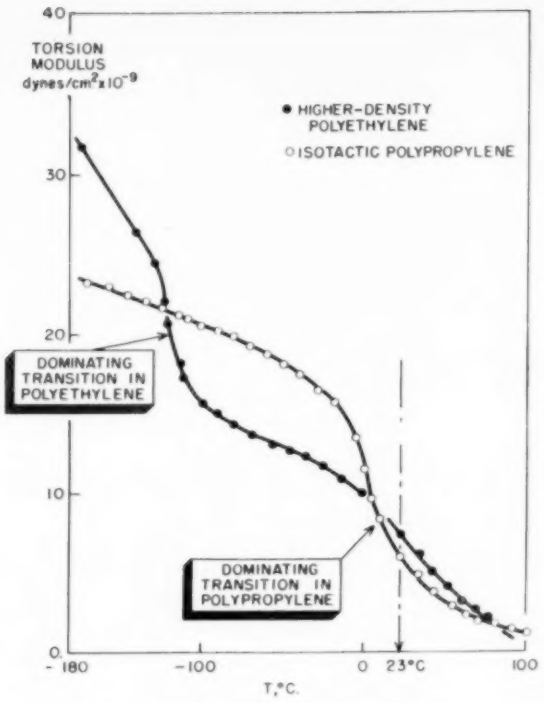

Figure 8. The variation with temperature of the torsion modulus and internal friction for three polypropylenes with different crystallinity.

TABLE I

Stiffness and Brittleness Temperature for Isotactic Polypropylene and Higher-Density Polyethylene

	Melt Index	Stiffness	Low Temperature Brittleness
Isotactic Polypropylene	1.09	135×10^3 psi	15°C
Higher-Density Polyethylene	1.15	115×10^3	<—100°C

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1. R. Buchdahl and L. E. Nielson, *J. Appl. Phys., 21,* 482 (1950).
2. K. Schmieder and K. Wolf, *Kolloid-Z. 127,* 65 (1952).
3. E. Jenckel, H. Hertog and E. Klein, *Z. Naturforsch., 8a,* 255 (1953).
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6. K. M. Sinnott, to be published.

★ ★ ★

Giulio Natta

Professor Giulio Natta received his degree in Chemical Engineering in 1924, and between 1926 and 1933 joined the faculty of the University of Pavia. During that time he became full Professor of General Chemistry. He was Professor of Physical Chemistry at the University of Rome and in 1938 joined the Institute of Industrial Chemistry at the Polytechnic Institute of Milan, of which he is now Director. Professor Natta is a member of the American Chemical Society, and the New York Academy of Science. He has authored more than 250 papers and holds a large number of patents.

Progress in Five Years of Research in Stereospecific Polymerization

Giulio Natta
Milan Polytechnic Institute

MORE THAN FOUR YEARS have elapsed since the first announcement of stereospecific polymerization of alpha olefins (Ref. 1). This discovery opened a new, immense field of research which attracted thousands of chemists and technicians in Europe, America and Asia.

This immense work has born remarkable fruits; most of them were foreseen by us when, in 1954, we announced the first highly stereospecific syntheses. In fact, we forecast the importance of sterical regularity on the properties of the obtained polymers.

Progress in Stereospecific Catalysis

Alpha-olefins: in our initial work with these olefins we clearly indicated the conditions for obtaining highly stereospecific catalysts, and polymers having a remarkable sterical purity (Ref. 2). Later work confirmed our early findings: highly stereospecific polymerization of alpha-olefins takes place with heterogeneous catalysts and the highest yields in isotactic polymers are obtained with the aid of catalysts formed by a crystalline component (preferably a halide of a highly electropositive transition metal in a low valence state) and a metal-organic compound of a strong electropositive metal having a very small ionic radius which yields complexes with the transition metal compounds; molecules of these complexes are tenaciously adsorbed on some points of the surface of the solid, crystalline component (Ref. 3).

Many workers have put on the same plane stereospecificity in the polymerization of α-olefins with the production of linear polymers of ethylene with the aid of Ziegler catalysts. Someone has also erroneously spoken of "isotactic polyethylene," without considering that isotacticity is a particular regularity in steric arrangement, connected with the possibility of existance of enantiomorphous forms of the monomeric units, owing to phenomena of stereoisomery. (Linear polyethylene cannot be isotactic since it does not contain regular sequences of asymmetric carbon atoms).

An accurate study of Ziegler type catalysts has demonstrated that perfectly linear polyethylenes, having high and very high molecular weights can be obtained with the aid of a great number of completely soluble catalysts (such as e.g. the products of the reaction between transition metal alcoholates and aluminum alkyls (Ref. 4) and certain metal-organic soluble complexes, some of which have been isolated by us in pure crystalline form (Ref. 5), while on the other hand, it is not possible to obtain with the aid of such soluble catalysts, isotactic poly-α-olefins.

Progress in the field of α-olefin polymerization has been achieved in the sense of regulating molecular weights and their distribution. Besides the methods

TABLE I

Stereospecific Polymerization of Propylene
(Temperature 75°C; Propylene Pressure 2.8 at; Solvent *n*-Heptane)

Catalyst			Percentage of isotactic polymer*	$[\eta_i]$
Metal-organic compounds mols		$TiCl_3$ mols		
$Al(C_2H_5)_3$	6.2×10^{-3}	3.1×10^{-3}	84.5	2.9
$Be(C_2H_5)_2$	9.5×10^{-3}	3.2×10^{-3}	96.0	2.7
$Be(C_2H_5)_2$	5.4×10^{-3}	4.5×10^{-3}	92.8	3.4
$Be(C_2H_5)_2\ 9.10^{-4} + Al(C_2H_5)_3 \cdot O(C_2H_5)_2$	4.2×10^{-3}	11.6×10^{-3}	96.0	2.5
$Be(C_2H_5)_2\ 9.10^{-4} + Al(C_2H_5)_3 \cdot O(C_2H_5)_2$	4.2×10^{-3}	11.6×10^{-3}	94.5	2.9
$[(C_2H_5)_2TiAl(C_2H_5)_2]_2$	4.15×10^{-3}	3.7×10^{-3}	96.7	3.9

* As % of isotactic polypropylene we assume the % of polymer not extractable with boiling *n*-heptane.

using hydrogen, many other processes have been found which are equally efficient, such as the one based on chain transfer with alkyl groups present in dissolved metal-organic compounds (Ref. 6).

The rate of such transfer is a function of the instantaneous concentration of the metal-alkyls present in solution (e.g. in the case of triethyl aluminum, it is a function of the square root of that concentration) (Ref. 7). Kinetic studies (Ref. 8), which were first developed on the α-$TiCl_3$-$Al(C_2H_5)_3$ system, have been later extended to other systems. These studies allowed us to explain the mechanism of chain transfer and chain termination processes which regulate molecular weight (Ref. 9).

In the case, e.g., of the regulation by a high concentration of aluminum trialkyls or hydrogen, the degree of polymerization depends, other conditions being equal, on the square root of the aluminum alkyl concentration or on the square root of the hydrogen partial pressure, and practically independent from the monomer partial pressure when it is higher than 1 atmosphere (Ref. 10):

$$\overline{DP} = \frac{1}{K_1 + K_2\sqrt{C_{Alk}} + K_3\sqrt{P_{H2}}}$$

where C_{Alk} indicates the aluminum alkyl concentration and P_{H2} the hydrogen partial pressure.

The regulation of molecular weight is of remarkable importance in particular applications of poly-α-olefins, in which melt viscosity plays an important role, e.g. for applications in the textile field. The use of highly pure and highly crystalline $TiCl_3$, and of metal-organic compounds yielding scarcely dissociable complexes permitted to obtain directly by polymerization, crude propylene polymers of remarkable sterical purity, containing more than 95% of macromolecules insoluble in boiling heptane, which are mostly insoluble also in boiling n-octane (Ref. 11).

The nature of the metal-organic compound has a remarkable influence on the sterical purity of the polymerizate. The more firmly the metal-organic compound is associated with the crystalline phase, the higher the stereospecificity.

If several metal-organic compounds are present at the same time, stereospecificity is determined by the one which is more strongly associated. This allows, for instance, to maintain the high stereospecificity which is observed when employing beryllium alkyls alone, even adding to small amounts of Be comopunds an excess of an Al-trialkyl-etherate (Ref. 12). Recently we have obtained high stereospecificities by replacing simple metal-organic compounds with other complexes which are chemisorbed by the surface of the transition metal compound (Ref. 13). (See Table I).

TABLE II

Physical Properties of Highly Isotactic Unoriented Polypropylene:
$[\eta_i] = (2\text{-}2.5)\ 100\ cm^3/g$

Specific gravity	0.915-0.920 g/cm³
Crystallinity (X-rays methods)	80-85%
Melting point (crystallographic microscope)	175-176°C
Yield strength, ASTM D 412	400-410 kg/cmq
Elongation at break, ASTM D 412	25-50%
Stiffness, ASTM D 747	15,000-16,000 kg/cmq
Hardness (Rockwell) ASTM D 785	R 110-115
Vicat softening point (5 kg load), DIN 57302	125-135°C

The analytical method already proposed by us in our earlier work (Ref. 2), according to which highly isotactic propylene polymers were isolated as residue after extraction of the crude with boiling heptane, was confirmed as valid in practice also from successive studies. In fact, a further fractionation, for instance by boiling octane, does not lead practically to remarkable variations in melting temperature, and yields fractions having different molecular weights but having, in practice, the same sterical purity (Ref. 14).

In Table II the properties of high isotactic polymers are listed. The crystallinity of highly isotactic polymers, M.P. 175-176°C, determined by X-rays, can reach in case the molecular weights are not too high, values of 80-85%.

Analytical determinations made at Polytechnic Institute of Milan demonstrated that the polymeric chains obtained in the presence of aluminum-alkyls result mostly bound to aluminum, and this is because the most important processes limiting the molecular weight of the polymer, when operating at not too high temperature, are processes kinetically comparable to a chain trans-

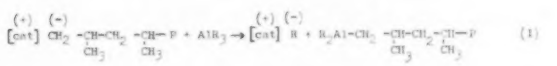
TABLE III

Isotactic and Stereoblock Polypropylenes

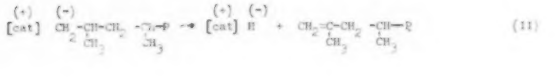
Solubility				
Extractable with Boiling	**Non Extractable with Boiling**	**Melting Temperature**	**X-Ray Crystallinity**	**Irregularities***
		°C	%	%
	trichloroethylene	176	75-85	0
	n-octane	174-175	65-68	0.6- 1.3
n-octane	2-ethylhexane	174-175	60-66	0.6- 1.3
2-ethylhexane	*n*-heptane	168-170	52-64	3.8- 5.1
n-heptane	*n*-hexane	147-159	41-54	10.8-18.0
n-hexane	*n*-pentane	110-135	25-37	25.2-39.4
n-pentane	diethylether	106-114	15-27	37.1-41.4

* Calculated according to Flory's theory, assuming a heat of fusion of 2600 cal/monomeric units.

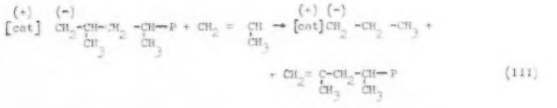
fer with the alkyl groups of the Al-alkyls in solution (I) and not the process of dissociation to hydride (II) and the chain transfer with the monomer (III). A great part of the chains remains therefore, during the whole polymerization, bound to the aluminum.



(I)



(II)

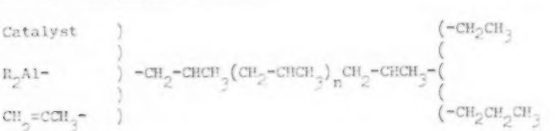


(III)

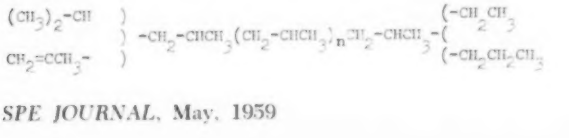
A characteristic feature of the polypropylenes, obtained with the aid of these catalysts after decomposition of the latter, is the presence in the polymeric chains of terminal groups of two different kinds. At one end of the chain there is usually an alkyl group, derived from the aluminum alkyl used in the preparation of the catalyst or a *n*-propyl group. At the other end of the chain there is a vinylidene group or an isopropyl group, this latter deriving from the decomposition, at the end of the polymerization, of the metal-organic compounds bound in the polymeric chains (Ref. 15).

In the polypropylenes produced with catalysts obtained from $TiCl_3 + Al(C_2H_5)_3$ the most frequent end groups are:

during the polymerization:



and after decomposition of the catalyst with alcohol or water:



If the molecular weight is regulated employing a high alkyl concentration, or by means of hydrogen, the number of isopropyl end-groups in the total polymer increases.

If the catalytic complex is easily dissociable, with separation from the active center of compounds containing metal alkyls, the inversions of steric configuration in the polymeric chains are more frequent (Ref. 17). The stereoblock polymers possess properties quite different from those of highly isotactic polymers and of atactic polymers. The percentage of sterical irregularities of the different polypropylene fractions can be calculated on the basis of the heat of fusion (2600 cal/mol unit) (Ref. 16), recently determined in the Institute (See Table III).

To a decrease in crystallinity, deriving from an increase in the number of inversions, corresponds a decrease of the melting temperature, but no remarkable variations in the second order transition, which depends on the non-crystalline part. With an increasing crystallinity, the unfavorable effects exerted by the amorphous part on the dynamic characteristics at temperatures near the second order transition, are reduced.

The second order transition of amorphous polypropylene is the highest among those of linear poly-α-olefins and may represent, in the case of low crystallinity polymers, an inconvenience for certain uses. The lowest second order transition is presented by linear polyethylene.

Copolymerization leads to irregularities, which cause a reduction in crystallinity and in melting temperature, in a way quite similar to what happens for polymers containing sterical irregularities; but while in the latter case the second order transition temperature is practically unchanged, in C_2—C_3 copolymers one can, on the contrary, observe a decrease in the second order transition temperature, which is the higher, the larger the ethylene content in the copolymer (Ref. 18). While in random copolymers of α-olefins with ethylene crystallinity tends to disappear when the ethylene content is higher than 20% and less than 80%, quite different are the properties of heteroblock copolymers. The ethylene-propylene copolymers possess remarkable crystallinities even for ethylene contents which, in an ideal copolymer, would lead to a complete disappearance of crystallinity. The ethylene-propylene copolymers having long heteroblocks present not only a good crystallinity, but also better properties at low temperature and a temperature of complete melting only a few degrees lower than that of pure isotactic polypropylene (Ref. 19).

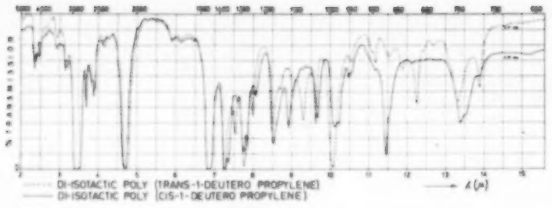


Figure 1.

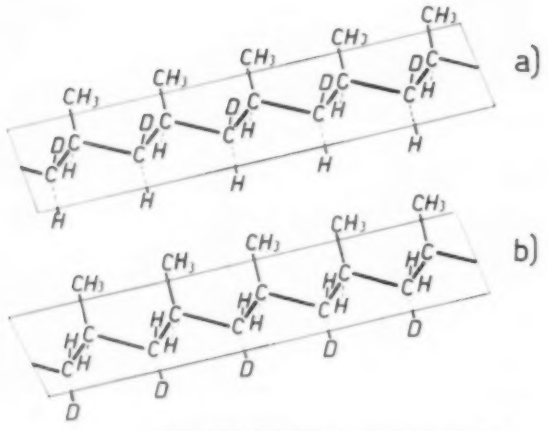


Figure 2.

The use of polymers having a high sterical purity is particularly important in the fiber field.

Four years of research in the laboratory were accompanied in Italy by the gradual development of a series of pilot plants of increasing capacity. These will be followed, in a short time, by commercial production of 10-million lb./year of textile fibers, which will be easily doubled. Staple fibers of different types will be produced and high-tenacity continuous yarns. They will be produced in a plant of the Montecatini Co. at Terni, whereas polypropylene for use as a plastic material is produced at Ferrara.

The Italian Industry early recognized the importance and vastness of the new fields which were opened by the discovery of stereospecific catalysis. It was thus necessary not only to expand the research work carried out at the Milan Polytechnic Institute, but also to create other research centers which have shared the tasks connected with the study of the stereospecific polymerization of α-olefins and of other monomers, of the preparation of copolymers, of the properties of the polymers and of the nature of the catalytic complexes. Besides the scientific studies in the University Laboratories of Milan, Pisa and others, the Research Institutes of the Montecatini Co., particularly those of Ferrara, Terni and Novara, are studying the commercial development of the new processes.

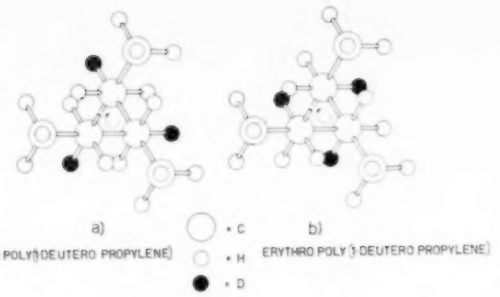


Figure 3.

Optical Active Isotactic Polymers

Very interesting results from the scientific viewpoint, have been achieved by Professor Pino at the University of Pisa in the preparation of polymers from optically active monomers. Starting from optically active olefins, polymers were obtained having a higher crystallinity than those obtained by racemic monomers and a different melting temperature. The optical activity of these polymers is very much higher than that of the corresponding monomers. In the case of poly-5-methyl-hexene-1, the optical activity is more than 100 times the optical activity of the monomer and is of opposite sign. The study of optically active catalysts and of their influence on stereospecificity and crystallinity was developed both at Milan and at Pisa with results of scientific interest which will form the object of papers to be published soon.

New Polymers of Di-Isotactic Type

At the Milan Polytechnic Institute, products belonging to a new class of stereo-ordered polymers have been prepared. These are polymers having a linear paraffinic chain of the –CHR-CHR′ type, in which carbon atoms linked to different substituting groups follow one another alternately. Crystalline, stereo-ordered polymers of this type were described by us as derived, respectively, from *cis* and *trans* $CHD = CHCH_3$ monomers (Ref. 20). When operating with stereospecific catalysts, and starting from the *cis* or from the *trans* stereoisomer, crystalline polymers are obtained which show certain differences in some of their physical properties. The infrared spectra, for instance, are remarkably different as can be seen from the attached drawings (Fig. 1).

New nomenclature problems have been faced, in order to characterize these new polymers, which we have called "di-isotactic." Polymers in which the configurations of both asymmetric carbon atoms are ordered, can occur in two different configurations. Suppose the chain stretched on a plane, we can, in the case of isotactic polymerization, have the two types of structure indicated in Fig. 2.

In Fig. 3 the projections of the spiral chains of the two stereoisomeric di-isotactic polymers, in the crystalline state, on a plane perpendicular to the *c* chain axis are represented. In Fig. 3 the left hand spiralized chains (*up* configuration) are represented; the right hand chains, which are also present in the crystals are different, being enantiomorphic (specular reflection).

In the projections shown in Fig. 3 the carbon atoms of the –CHD– groups are not visible, because they are covered (by the tertiary carbon atoms of the $-CHCH_3$ groups).

We propose the following nomenclature: "threo-di-isotactic" for the polymers of one of the two types indicated in Fig. 3, for which, suppose the chain stretched on a plane, all the substituting groups are on the same side of the plane; and "erytro-di-isotactic" for those in which one substituting group is on one side, while the other is on the other side. Both these isomers were isolated by us, as well as the mono-isotactic polymers obtained by random copolymerizantion of a mixture of the *cis* and *trans* isomers of the monomer.

Crystallinity of Isotactic Polymers

Isotacticity is a property depending only on the steric structure of the main chain and is not necessarily connected with crystallinity. Therefore, the extent of crystallinity is not sufficient to indicate the degree of isotacticity. The degree of crystallinity depends on the heat and mechanical treatments undergone by the polymer and reaches values which may result very differently according to the method employed for its determination.

A crystalline isotactic polymer remains isotactic even in the liquid state, when heated at a temperature higher than that of melting of the crystals; the same happens also at low temperature if, by rapid quenching, its normal crystallization is hindered. In this case, below the second order transition temperature, many isotactic polymers can be obtained as an amorphous glass, only slightly different, in certain physical properties, from a linear atactic polymer. In the case of isotactic polypropylene, an unstable crystalline smectic modification can be obtained by quenching, having different lattice structure and low density (0.88). This modification presents approximately the same infrared spectrum, and shows a crystallinity which is only slightly lower than for the stable crystalline modification obtained from the same sample by annealing (Figs. 4 and 5).

The X-ray examination shows that the unstable modification has the same helical chain structure and the same identity period along the chain as the stable modification, but a different (random) packing of the enantiomorphous chains in the tridimensional lattice (Ref. 21). This explains the possibility of obtaining from highly isotactic polypropylene, films which are more transparent than polyethylene films. In this latter, in fact, a considerable difference in the specific gravity and in the diffraction index between amorphous and crystalline polymer makes it impossible to obtain highly transparent films, because they contain regions of different crystallinity having dimensions greater than the wave length of light.

Research work recently performed at the Milan Polytechnic Institute, and the results of which are in press, have demonstrated that the crystallinity bands in the 2-15 microns field in the infrared spectra of isotactic polymers (contrary to what happens in other spiralized polymers, such as the proteins and cellulose) are only due to vibrations connected with ternary helix conformation of the macromolecule and not to the interactions between monomeric units of different chains.

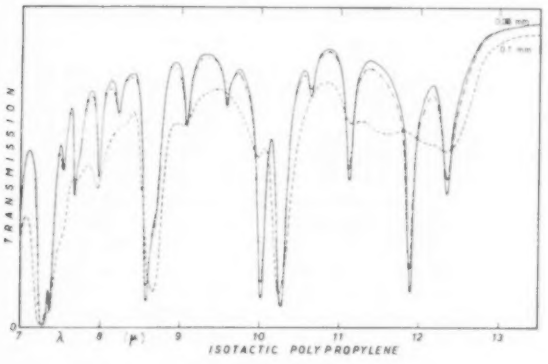


Figure 4.

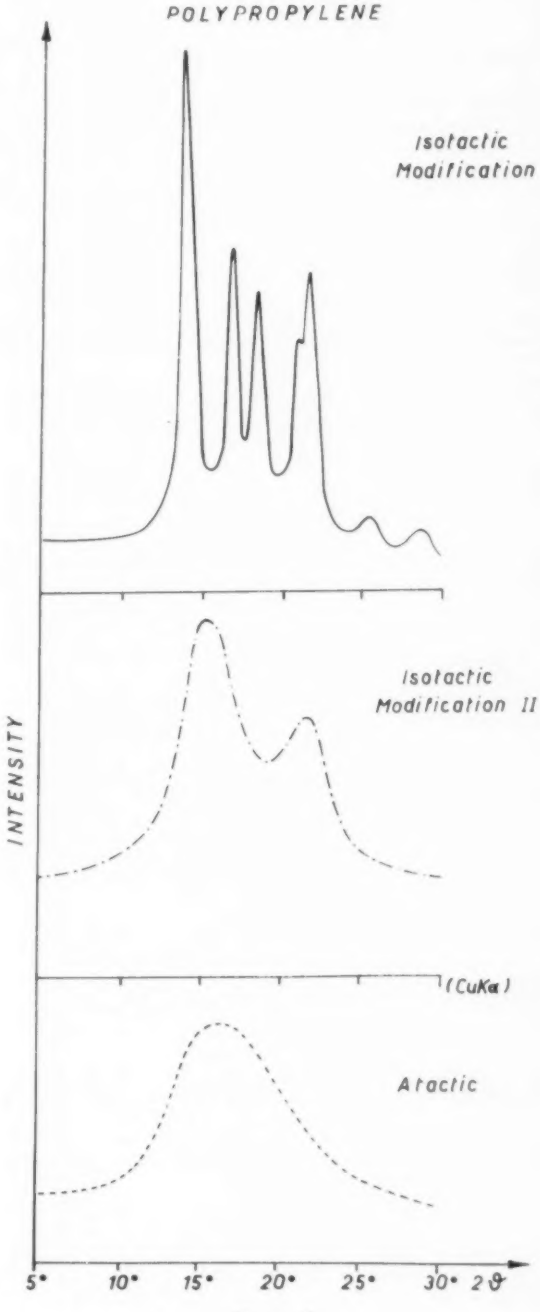


Figure 5.

TABLE IV

Isotactic, Crystalline Aromatic Polymers.

Monomer	Intrinsic Viscosity	Melting Point °C
styrene	3.5	240
o-methyl-styrene	—	>360
m- " "	3.9	215
2-4 dimethyl-styrene	3.5	310
2-5 " "	3.5	330
3-4 " "	3.2	240
3-5 " "	2.6	290
o-fluoro-styrene	2.3	270
p- " "	2.0	265
2-methyl-fluoro-styrene	—	>360
3-vinyl-naphtalene	2.3	360

Infrared bands due to crystallinity can therefore be observed also in the absence of a regular association of several chains, (which is necessary to impart a crystallinity detectable by X-rays) provided that there exists a regular spiralization in each chain. Moreover, it may be observed that in certain random isotactic aromatic copolymers, which are crystalline by X-rays, but where different "isomorphous" (e.g. vicariable in the chain) monomeric units follow each other along the chain, the infrared bands of crystallinity disappear (Ref. 22).

The absence of a crystallinity, depending on the structure of the main chain, in α-olefin isotactic polymers having linear side chains with more than four carbon atoms, demonstrates that crystallinity by itself is not sufficient to define the isotacticity of a polymer. The copolymerization with stereospecific catalysts gives different results as to the crystallinity, according to the type of monomers employed and the operating conditions.

Monomeric units having shape and dimension only silghtly different from each other can vicariate along the chain in a quite similar way to what occurs in the lattices of solid solutions between isomorphous substances, and thus yield crystalline copolymers with lattice constants slightly different from those of the homopolymer of the prevalent monomer. As in the case of tridimensional lattices of low molecular weight substances, isomorphism and iso-dimorphism phenomena can occur also in linear spiralized polymeric chains, provided the monomeric units deriving from different monomers have very similar structure and dimensions, and can thus substitute each other varying only slightly the identity period and the cross-sectional area of the spiralized chain. Phenomena of iso-dimorphism are expected to occur when the two homopolymers can crystallize in different forms (e.g. with identity periods containing a different number of monomeric units). When, however, the monomeric units do not show "isomorphism," crystallinity may occur in different cases as follows: 1. When the percent of monomeric units which is copolymerized, is small; 2. When copolymerization does not occur randomly, but forming long isotactic blocks.

The melting temperature of isotactic homopolymers depends, first of all, on steric factors and is not related with the melting point of the monomers. Branched olefins have melting temperatures lower than those of linear olefins having the same number of carbon atoms, but the isotactic polymers of many branched olefins

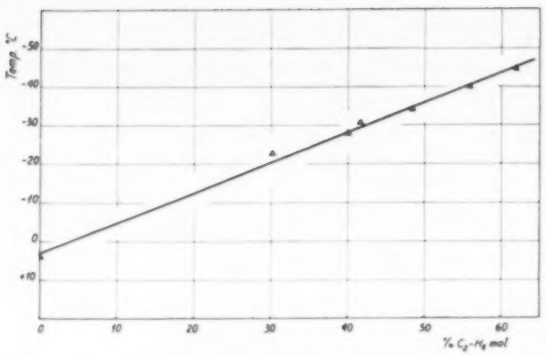


Figure 6.

have melting points much higher than those of the corresponding linear olefins (Ref. 23).

A similar behavior is noted also with certain isotactic aromatic polymers (See Table IV). Isotactic polymers having high crystallinity were obtained also from certain aromatic monomers; some of these polymers possess the advantage, in respect of normal isotactic polystyrene, of a higher crystallinity and a higher crystallization rate (Ref. 24). Crystallinity in isotactic polymers is hindered in those cases in which the side chains are very mobile or when, even if not mobile, they present a bulk which does not permit of a good, compact packing, without large bond deformations or a too close approaching of the atoms to each other in contrast with Van der Waals distances.

It can be affirmed that in all cases in which hydrogen bridges or attractions of a chemical nature favoring the packing of chains are absent, a polymer cannot crystallize when the possible packings of the chains, taking into account the distances permitted by Van der Waals forces, would lead to the formation of crystals having specific gravities lower than those possessed by the same polymer in the liquid or glassy state. This is why many isotactic polymers do not crystallize at all, or crystallize only with difficulty.

We must, however, distinguish between the impossibility to crystallize and the difficulty to crystallize. The latter can be due to sterical hindrances, such as interactions between the main chain and side groups. The difficulties encountered in the crystallization of isotactic polymethacrylates are caused by the low mobility of the chain and find their counterpart in some aromatic polymers which also crystallize with difficulty. Irregularities in the chain lead to a decrease in crystallinity. The same results are obtained, as far as crystallinity is concerned, by introducing sterical irregularities (gradually transforming the isotactic polymer into a stereoblock polymer and into an atactic polymer) or by copolymerization with different monomeric units.

Quite different is the behavior, as far as the second order transition is concerned. An atactic polymer possesses approximately the same second order transition as the not crystallized portion of an isotactic polymer or of a stereoblock polymer. A copolymer presents a second order transition which is intermediate between those of the two monomers. This explains the variation of the mechanical properties of ethylene-propylene copolymers with composition. Fig. 6 shows the minimum rebound temperature of the random copolymers. This is the reason of the great interest presented in the field of elastomers by copolymers containing ethylene, presenting, as said, a very low second order transition.

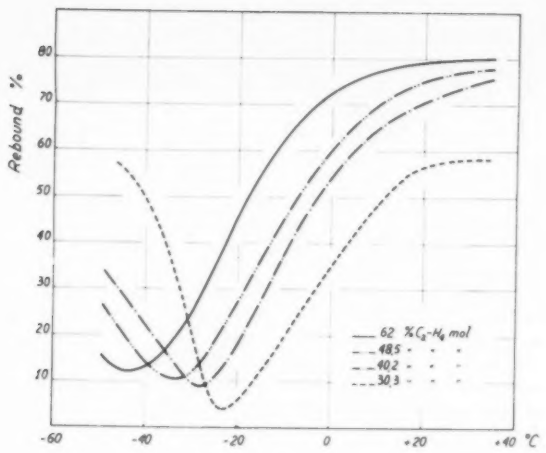


Figure 7.

Fig. 7 shows the rebound properties of the random C_2—C_3 copolymers having different composition, as a function of temperature. It is important to note that when the copolymer obtained with the aid of highly stereospecific catalysts contains such a number of irregularities as to hinder crystallization, many of its properties (particularly the mechanical properties) are practically identical to those of a linear head-to-tail copolymer having the same composition, but obtained by means of a catalyst having low or no stereospecificity. The absence of a regular spiralization of the main chain causes the absence of crystallinity bands in the infrared spectra.

When working with stereospecific catalysts, the monomer's reactivity ratios are nearer to each other and this is an advantage in the polymerization process, making it easier to obtain homogeneous copolymers (Ref. 25). (See Table V).

A characteristic feature of coordinated, anionic copolymerization, as well as of other ionic polymerizations, is the fact that the product of reactivity ratios presents a value of 1 or near 1. This has been verified also in the case of copolymerization of aromatic monomers (Ref. 26). (See Table VI).

Isotactic Polymers of Various Non-Hydrocarbon Monomers

The same catalysts which polymerize in a stereospecific way α-olefins, behave similarly with vinyl monomers containing silicon or tin in the side chain (Ref. 27) and with certain monomers containing halogen atoms linked to aromatic groups.

The use of heterogeneous catalysts is necessary for these stereospecific polymerizations as we have already pointed out for α-olefins. The particular sterical orientation of the monomeric units is probably related with the structure of the activated, intermediate complex formed by the monomer with the catalyst.

Polarization of the vinyl double bond, the preferred orientation of the intermediate product and the constance in the type of opening of the double bond are related with a sterically univocal chemisorption of the monomer on an active center formed by an asymmetric metal-organic complex which is part of a solid, ordered surface connected with a layer lattice. The study of the polymerization of *cis* and *trans* $CHD = CH \cdot CH_3$

TABLE V

Ethylene and Propylene Reactivity Ratios in Copolymerization in the Presence of Catalysts Prepared from Trialkyl Aluminum and Different Transition Metal Halides.

Metal halide	$^rC_2H_4$	$^rC_3H_6$	$^rC_2H_4 \cdot {}^rC_3H_6$
$VOCl_3$	17.95	0.065	1.17
VCl_4	7.08	0.088	0.63
VCl_3	5.61	0.145	0.81
$TiCl_4$	33.36	0.032	1.07
$TiCl_3$	15.72	0.110	1.73
$TiCl_2$	15.72	0.110	1.73

TABLE VI

Reactivity Ratios of Some Vinyl Aromatic Monomers in Copolymerization in the Presence of Catalysts Prepared from $TiCl_4$ and $Al(C_2H_5)_3$

Monomers	r_1	r_2	$r_1 \cdot r_2$
styrene-*p*-methylstyrene	0.82	1.15	0.95
" *m*-methylstyrene	2.0	0.5	1.0
" *p*-ethylstyrene	1.0	1.0	1.0
" *p*-chlorostyrene	2.2	0.5	1.1

monomers, forming "di-isotactic" polymers, makes it possible to affirm that, in stereospecific catalysis, not only the mode of presentation of the monomer on the catalyst, but also the type of opening of the double bond, and therefore the configuration of both the —CHD and the $—CH \cdot CH_3$ groups, is determined. Quite different can be the behavior of monomers which, besides a vinyl double bond, contain another double bond conjugated with the first, or an atom having a lone electron pair able to associate itself chemically with the catalytic complex.

In these cases the preferential orientation, necessary for a stereospecific polymerization, can be caused by the coexistence of two interactions, the one given by the vinyl group and the other given by the other group or atom conjugated with the first (Ref. 28). These interactions impose a particular structure to the intermediate activated complex. This is why it is possible in these cases to have stereospecific polymerizations also with the aid of soluble catalysts.

In our early investigation we had obtained by homogeneous catalysis crystalline isotactic and syndiotactic polymers, with 1-2 enchainment, and atactic, amorphous polymers of diolefins (Ref. 29).

Recently, T. G. Fox and coworkers of the Rohm & Haas Co. have disclosed the preparation of isotactic and syndiotactic polymers of methacrylates, by means of anionic polymerization using soluble catalysts, formed by metal-organic compounds of lithium (Ref. 30). J. D. Stroupe and H. E. Hughes have established the structure of the isotactic polymers thus obtained (Ref. 31). Isotactic polymers of vinyl ethers were prepared by us (Ref. 28) with the aid of various soluble catalysts of a more or less cationic type, different from those initially used by Schildknecht (Ref. 32) (See Table VII). In many cases we obtained higher crystallinity.

The knowledge of these new types of stereospecific catalysts permits us to explain better the mechanism of stereospecific polymerization. In a preceding paper, I had defined as anionic, coordinated polymerization the one based on the use of catalysts formed by complexes in which metal-organic compounds of strongly electro-

positive metals and low-valence compounds of transition metals are contained (Ref. 33). In the United States there is a tendency to call this type of polymerization "coordinated," eliminating the term "anionic."

Such a simplification may lead to some misunderstandings, since there are processes of cationic polymerization which should be considered as coordinated, owing to the fact that the catalysts are complexes. It is not possible, on the other hand, to limit ionic polymerization to only those cases in which a complete dissociation in ions takes place, because the greatest part of the polymerization processes which are usually considered as typically cationic do not satisfy this requirement.

The attribute "anionic" or "cationic" for coordinated polymerization should be put in relationship with the polarity of the terminal carbon atom of the polymer linked to the catalytic complex. If this atom presents a negative polarity, the catalysis should be considered of the anionic, coordinated type. If it presents, on the contrary, a positive polarity, the catalysis should be considered of the cationic, coordinated type.

The α-olefin polymers obtained in conditions in which a chain transfer with the monomer takes place, generally contain in the first case macromolecules having a vinylidene end group; in the second case they mostly contain an internal double bond or a vinyl group.

TABLE VII

Polymerization of Isobutylvinylether at −78°C in Homogeneous Phase, in the Presence of Different Aluminum Compounds.

Catalyst	Properties of the polymer
$Al(C_2H_5)_3$	no polymer
$Al(C_2H_5)_2Cl$	crystalline, substantially insoluble in boiling acetone, $[\eta]$ in toluene at 30°C = 2.1
$Al(C_2H_5)Cl_2$	crystalline, substantially insoluble in boiling acetone, $[\eta]$ in toluene at 30°C = 2.3
$AlBr_3$	almost completely amorphous, soluble in boiling acetone, $[\eta]$ in toluene at 30°C = 0.9

There are typically cationic complexes, such as those obtained from $AlCl_3$ or $TiCl_4$ and an alkyl-halide, and typically anionic complexes, such as those obtained from titanium di-or trivalent salts and lithium, beryllium or aluminum alkyls.

There are, furthermore, complexes showing intermediate properties between those of cationic and anionic catalysts. The complexes formed by low-valence compounds of transition metals with $AlCl_3$ possess properties which are nearer to those of cationic catalysts, while the complexes of the same type obtained with metal-alkyl-halides present intermediate properties. Some of those complexes show stereospecific properties. For instance, the $AlCl_3$-$Ti(Cp)_2Cl$ complex polymerizes vinyl ethers to crystalline polymers (Ref. 34).

When the chlorine content is decreased through partial to total substitution by alkyl groups, the tendency to polymerize vinyl ethers also decreases, while the ability to polymerize ethylene increases (See Table VIII). Complexes richer in alkyl groups do polymerize also α-olefins, if a suitable crystalline support is present.

Stereoisomeric Polymers of Diolefins

Our research work in the field of diolefin polymerization by catalysts containing aluminum metal-organic compounds began with a study of butadiene polymerization by means of a catalyst formed of $Al(Et)_3$ only.

Together with the discovery of highly stereospecific catalysts for the polymerization of α-olefins, the discovery of highly stereospecific catalysts for the polymerization of diolefins was developed. The general conditions for the polymerization of diolefins with catalysts of that type were indicated by us.

Thus the first crystalline butadiene and isoprene polymers, with high content in *trans*, 1-4 enchained units were obtained and their preparation is the subject of patents. With the same catalysts which are highly stereospecific in the polymerization of α-olefins, we easily obtained highly pure (>99%) *trans*, 1-4 polymers (Ref. 35). Using catalysts formed by soluble complexes containing O, N, etc., we similarly obtained isotactic, syndiotactic, and atactic polymers having a 1-2 enchainment (Ref. 29).

We also succeeded in obtaining high yields of crystalline butadiene polymers having a high content of *cis*, 1-4 units. The metal-organic catalysts containing titanium, prepared by us in our early work, even if

TABLE VIII

Catalytic Activity of Dimetallic Complexes in the Polymerization of Ethylene and of Isobutyl-Vinyl-Ether.

	Polymerization of isobutyl-vinyl-ether						Polymerization of ethylene			
Catalyst	Mols of monomer / Mols of catalyst	Temp. °C	Time hr.	Yield	$[\eta]$ in toluene at 30°C	Polymers properties	Time hr.	Press. atm.	Temp. °C	g of crystalline polyethylene/mol of catalyst
$(C_5H_5)_2TiCl_2AlCl_2$	400	−78	2	97	2.03	see under A*	21	40	85	690
$(C_5H_5)_2TiCl_2AlClC_2H_5$	290	−78	3	34	2.15	see under B**	8	40	95	3400
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	35	−78	15	0	—	—	8	40	95	3700

* A = Crystalline polymer. Fraction insoluble in boiling acetone = 91%
** B = Crystalline polymer. Fraction insoluble in boiling acetone = 55%

TABLE IX

Physical Properties of Vulcanized Polybutadienes with High Content in *cis*,1-4 Stereoisomer (Pure Gum Recipe).

cis, 1-4 content	88-90%	96-98%
Mooney viscosity, ML 4	90-95	70-80
Tensile stress, psi	800-1100	2500-2800
Elongation at break, %	900-1000	850-950
Modulus at 300% elong., psi	140-180	140-180
Resilience at 20°C, %	80-85	85-88
Hardness, Shore A	45-50	45-50

Compounding recipe:

Polybutadiene	100
Stearic Acid	2
Zinc oxide	3
Sulphur	1
Vulcafor MBTS (di-2-benzothiazyl disulphide)	1.3
Nonox D (phenyl-β-naphtylamine)	1

Cure: 145°C x 45 min.

TABLE X

Physical Properties of Vulcanized Polybutadienes with Different Content in *cis*, 1-4 Stereoisomer (Carbon Black Recipe).

cis, 1-4 content	88-90%	96-98%
Mooney viscosity, ML 4 of raw polymer	50-55	45-50
Tensile stress, psi	2200-2500	3300-3600
Modulus at 300% elong., psi	1000-1100	1100-1300
Elongation at break, %	500-600	450-550
Resilience at 20°C, %	55-60	60-65
Resilience at 90°C, %	60-65	65-70
Hardness, Shore A	60-65	60-65

Compounding recipe:

Polybutadiene	100
Stearic acid	2
Zinc oxide	5
Vulcan 3 (HAF)	50
Sulphur	2
Vulcafor MBTS (di-2-benzothiazyl disulphide)	1
Nonox D (phenyl-β-naphthylamine)	1

Cure: 145°C x 45 min.

prepared with particular Al-Ti ratios, always yield crude polymers containing, besides the *cis*, 1-4 units, also *trans*, 1-4 and 1-2 units.

The use of catalysts prepared from TiI_4 as described by the Phillips Co. (Ref. 36) permits us to increase the total content of *cis*, 1-4 units in comparison with the crude polymers obtained from $TiCl_4$, but not to obtain pure, crystalline polymers.

Early in our investigation we had assumed that the poor stereospecificity of catalysts obtained from soluble titanium halides was due to the fact that such catalysts do not present an homogeneous composition and contain active centers of different types and different stereospecific activities. This assumption was confirmed by low temperature fractionation, which enabled us to isolate from their solutions, by means of fractional crystallization at −30 to −40°C. crystalline *cis*, 1-4 butadiene polymers, to establish their lattice structure and to observe their ability to crystallize, as does natural rubber, under stretch at room temperature or higher (Ref. 37).

Using catalysts of a particular type, containing only one type of active center, crude butadiene polymers having a *cis*, 1-4 content higher than 97% were obtained, both at the Donegani Institute of Novara and at Milan. The influence of steric purity on the properties is enormous (See Tables IX and X).

Polybutadiene, vulcanized in the absence of reinforcing fillers, yields a rubber which has low initial elastic modulus and high tensile strength, only if it is able to acquire high crystallinity under stretch. *Cis*, 1-4 highly pure polybutadiene is the product nearest to *cis*, 1-4 polyisoprene (i.e. to natural rubber) in elastic properties. One of the difficulties encountered in the use of polybutadiene was the fact that high molecular weight polymers are difficult to process and difficult to depolymerize by thermal or mechanical treatments. It is now possible to regulate the molecular weight directly in the polymerization step and also to achieve a planned distribution of the molecular weights.

The infrared spectra of isotactic and syndiotactic 1, 2 and of *trans*-1, 4 polybutadienes are reported in Figs. 8, 9 and 10 respectively. We think it useful to report these infrared spectra here since, examining the literature, one sees that different coefficients have been used in the United States and in Europe to determine the

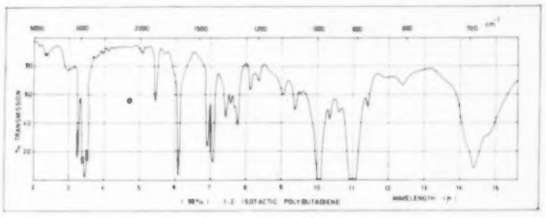


Figure 8.

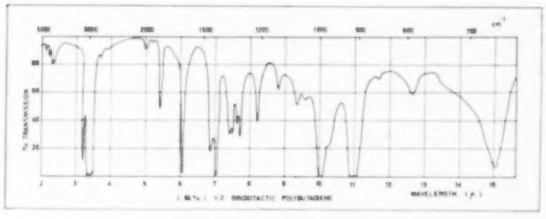


Figure 9.

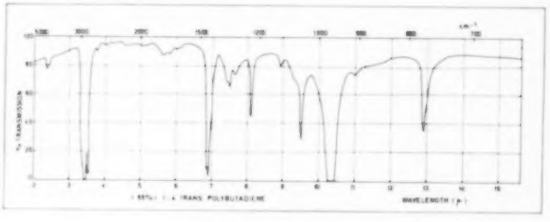


Figure 10.

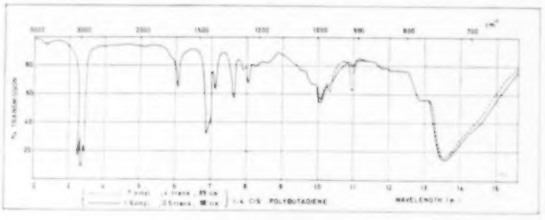


Figure 11.

stereoisomeric purity of the polybutadienes by infrared methods. Thus, infrared spectra of butadiene polymers have been reported (Ref. 38), from which the authors have concluded to a *cis*, 1-4 content of 95%; when interpreting said spectra according to our coefficients, a *cis*, 1-4 content of only about 88% results.

In Fig. 11 the infrared spectra of two samples, having different *cis*, 1-4 contents are compared. The contents of the different structures as determined with our coefficients are indicated.

The maximum practical interest is shown by highly pure *cis*-1, 4 polymers having a controlled molecular weight. They present good processability and very good mechanical properties, even in the absence of reinforcing fillers, and very good resiliency even at low temperature.

The study of the polymerization of diolefins and of other monomers, with the production of crystalline polymers of different steric structure, demonstrates that the difference in properties between various polymers of different structure is due not only to the fact that they present crystallinity or not, but depends in a determining way on the specific type of steric structure.

In all cases where different steric configurations are possible, it is not sufficient, in order to define the polymer, to indicate that it is able to crystallize, but it is necessary to establish the type of sterical regularity and its sterical purity.

The same polymer having a given sterical configuration and a given sterical purity, and which can be obtained in different crystalline modifications, can show different properties in dependence of the actual crystalline structure (e.g. in the case of polypropylene, polybutene, *trans*-1, 4 polybutadiene), but the differences in mechanical properties deriving from the type of crystal structure are less important than those deriving from differences in the steric configuration.

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A Visual Analysis of Flow and Mixing in Extruder Screws

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THE FLOW BEHAVIOR of thermoplastic materials in the channel of an extruder screw has been studied by a number of observers both in this country and abroad. Several simplifying assumptions have been proposed and the problem divided into two general categories: one of isothermal conditions of the molten material in the forward end of the machine and the other of plug flow of the solid, granular material in the feed and compression sections of the screw. Mechanisms occurring in the transition from solid to melt have usually been recognized as extremely complex, tending to defy treatment on a theoretical or mathematical basis.

This paper describes a method for visualizing the flow of individual particles during melting and the contributions of pressure and other operating variables to the ultimate fusion and mixing of the molten particles into a homogeneous extruded product.

Summary

Graphic illustrations of flow, fluxing and mixing in extruder screws are obtained by stopping the extruder and removing the filled screw. Flow paths traced by colored polyethylene and plasticized PVC particles in their travel through the channel are easily observed in this manner.

A basic mechanism of fluxing was found to be common to all screw types. Particles are conveyed rapidly along the screw surface until they become subjected to shearing action between the root of the screw and a thin skin of molten material along the barrel. They are then smeared around the barrel in a direction normal to the screw axis until they meet the leading edge of the advancing thread. Here they are mixed with previously molten material, forced downward into the channel initiating a helical circulating path. This circulating flow is confined to the rear portion of the channel in each turn, the forward portion being filled largely with unfluxed material. The width of the fluxed and circulating band gradually increases toward the exit end of the screw. Under ideal conditions, this mechanism produces complete fluxing and a homogeneous product before discharge from the screw, but this condition frequently is not realized, particularly if the channel is too deep at the exit end.

Fluxing and mixing are accelerated by decreasing the channel depth, by increasing the back pressure or by cooling the screw, these mechanisms being clearly indicated in the illustrations. Lubricants delay fluxing by reducing adhesion to the barrel and screw surfaces. Excessive lubricity completely disrupts the normal fluxing and circulating flow behaviors to the extent that essentially no mixing takes place.

Transition from Solid to Melt

Mechanisms taking place in the compression or melting sections of the screw do not appear to have been investigated either from a theoretical or experimental point of view. We will not attempt to analyze the flow conditions in this region mathematically, but have employed an experimental technique which permits visual observation of flow paths taken by individual particles. This work was carried out in a 2.0″ diameter, 15/1 L/D ratio, steam-heated extruder feeding into a needle-type pressure control valve and a 3/16″ diameter rod die. Fig. 1 shows a schematic diagram of the described system. An 8.0″ diameter air cylinder, developing a force of about 4,000 lbs., is mounted behind the machine to

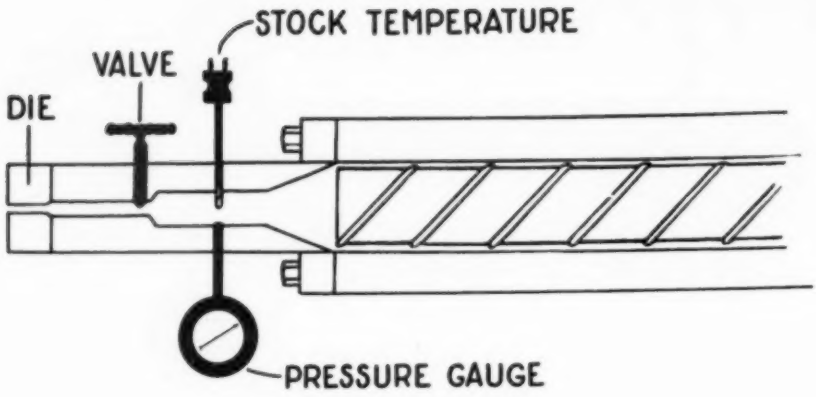

Figure 1. Extruder setup.

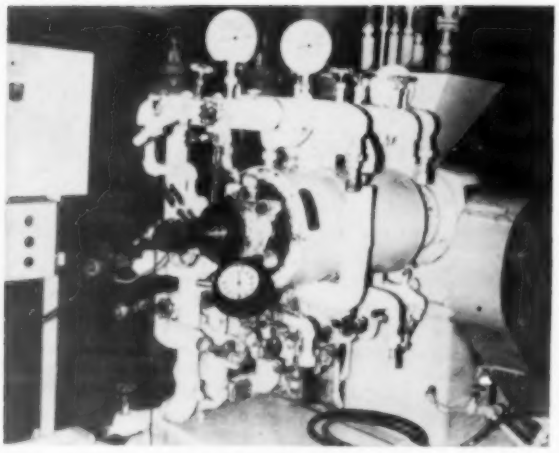

Figure 2. Extrusion apparatus.

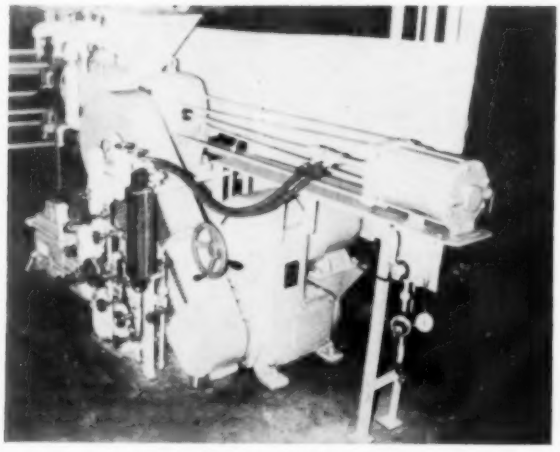

Figure 3. Screw push-out system.

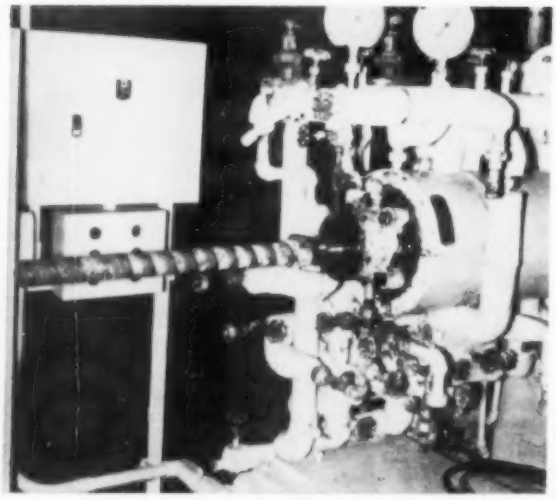

Figure 4. Screw in process of removal.

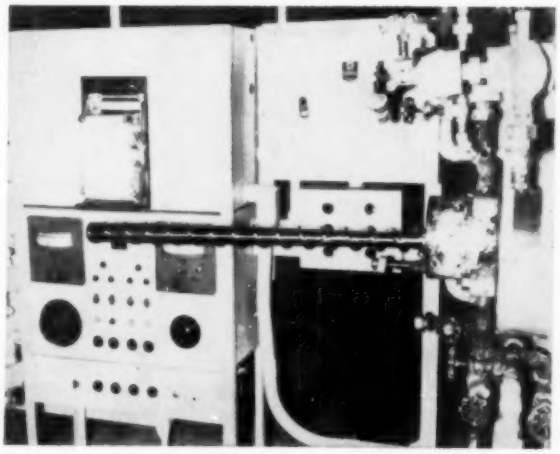

Figure 5. Screw A.

push out the filled screw. Figs. 2 and 3 show photographs of the equipment. A screw in the process of removal is pictured in Fig. 4.

Experimental Procedure

When the machine has been stabilized at a desired set of operating conditions, the drive motor is stopped and cooling water applied immediately both to the screw and the barrel. After cooling for about 10 min., the head is removed from the machine and air at about 80 psi line pressure applied to the air cylinder. This normally will not move the screw. Heat is then reapplied to the barrel while still retaining the cooling water on the screw. When the barrel reaches the proper release temperature, the screw will start to move forward. The 10" stroke of the cylinder employed necessitates insertion of short additional lengths of push rod to accomplish the full length of screw travel. Continued cooling of the screw during push-out is essential. If this is not done the material in the channel is remelted and tends to pile up at the rear of each flight as the screw moves out of the barrel. After removal from the barrel and a few minutes futher cooling, the material helix can be unwrapped from the screw.

Two plastic materials were studied. One was a tumbled blend of Bakelite Brand DYNH (2.0 Melt Index) polyethylene pellets with about 5% of a red pigmented polyethylene. The other was a 30/1 blend of a 35% plasticized polyvinyl chloride compound with a brown pigmented material of the same general composition. Under conditions of good mixing in the screw, these materials extruded with a uniform red or brown color.

The screw employed for most of the work was a typical metering type screw having a channel depth of 0.375" at the feed hopper, a continuously decreasing depth in the compression section and a depth of 0.120" in the three-turn metering section. This screw is pictured in Fig. 5 and is designated as screw "A."

EXPERIMENTAL RESULTS

Vinyl Compound

A typical plastic helix, after removal from the screw, is shown for the vinyl compound in the upper view of Fig. 9. An uncoiled helix showing the inner surface is pictured in the lower view. This photograph represents a neutral screw operating condition at 48 rpm with barrel temperatures of 177-188°C (350°-370°F) and a head pressure of 1500 psi.

Several characteristic effects are noted in Fig. 6. A thin skin of molten material forms along the barrel surface well back in the screw, but the bulk of the pellets are conveyed rapidly along the screw surface. As the channel depth decreases and individual pellets become subjected to shearing action between the root of the screw and the molten skin along the barrel, they are picked up and smeared straight around the barrel in a direction normal to the screw axis. As they meet the leading edge of the advancing flight they are mixed with previously molten material in this area, forced downward toward the root of the screw and start the helical circulating flow visualized by the theoretical analysts. This circulating flow, however, is confined to the rear portion of the channel in each turn. The forward portion is still filled largely with unfluxed material. The width of the fluxed and circulating band gradually increases toward the exit end of the screw, as indicated by the dark areas in the lower view. Actually, the conditions employed in this example were not favorable for complete mixing. While a fairly uniform color distribution was reached along the screw surface in the metering section, fluxed, but unmixed

Figure 6. Vinyl compound helix from screw A.

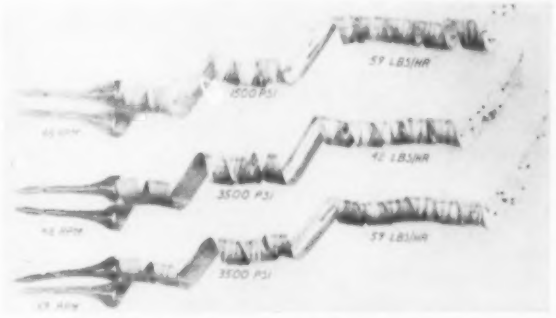

Figure 7. Effect of presure and extrusion rate.

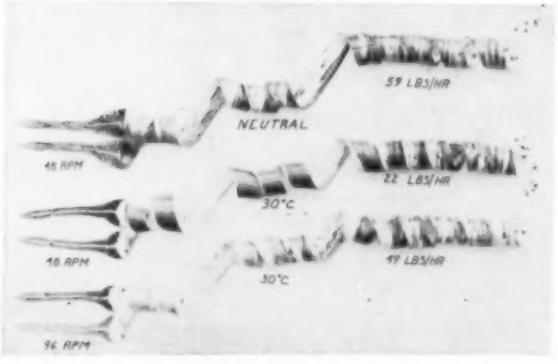

Figure 8. Effect of screw cooling.

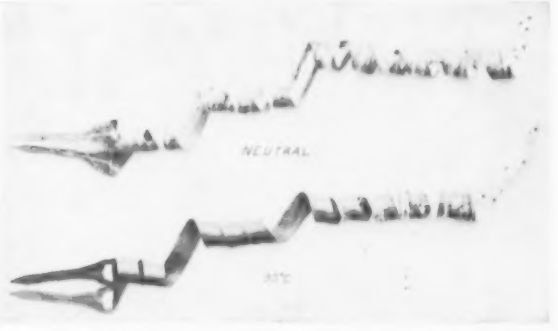

Figure 9. Effect of screw cooling after long running time.

Figure 10. Polyethylene—Effect of pressure.

Figure 11. Polyethylene—Effect of screw cooling.

material was still moving off the end of the screw in the forward portion of the channel near the barrel surface. The better mixing along the screw surface at the exit end is believed to be the contribution of back flow in this area. Poor mixing was also evident in the head adaptor, in the channel leading to the valve and in the extruded product. This is clearly indicated in the adaptor section in the upper view of Fig. 6.

Effect of Pressure

The effect of increased head pressure, created by reducing the valve orifice, is shown in Fig. 7. In all of these samples the operating conditions were established first with the natural, uncolored vinyl compound. The natural and brown blend was then introduced and the run continued for only a few minutes after the initial showing of brown color in the extrudate. This gives an added evaluation of material hangup as indicated by the white material still adhering to the end of the screw and the walls of the adaptor. Raising the pressure from 1500 to 3500 psi without increasing the screw speed, as shown in the center sample of Fig. 10, causes earlier fluxing and a definite volume of well-mixed material in the exit end of the screw. The extruded rod has a uniform brown color except for a very small central streak of white material which is gradually being pulled off the flat end of the screw. With continued extrusion of the color mixture this white streak and the white layer along the wall of the adaptor eventually disappear.

The pressure increase also caused a reduction in output rate from 59 to 42 lbs./hr. The screw speed was then raised to 69 rpm at the higher pressure to return to the original rate. The bottom sample of Fig. 7 illustrates this condition. It is seen that the volume of well-mixed material at the exit end has been reduced, but that the degree of mixing in the adaptor and the extruded product is considerably better than in the top sample which was run at an equal rate at the lower pressure.

Effect of Screw Cooling

Screw cooling is frequently employed to effect improvements in mixing and product quality. The manner in which this is accomplished is indicated in the center and bottom samples of Fig. 8, where the screw was cooled with water at an average temperature of 30°C (86°F) and a flow rate of 1.5 gal./min. The head pressure, in each case, was 1500 psi. Again, the uncolored material was extruded first and followed, for a few minutes, by the color blend.

In the center sample it is noted that a layer of the earlier, white material adheres to the screw while the

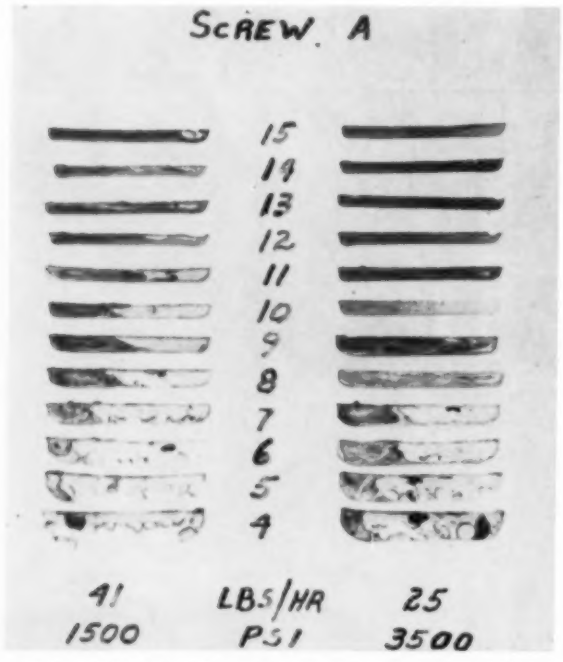

Figure 12. Effect of pressure at constant screw speed.

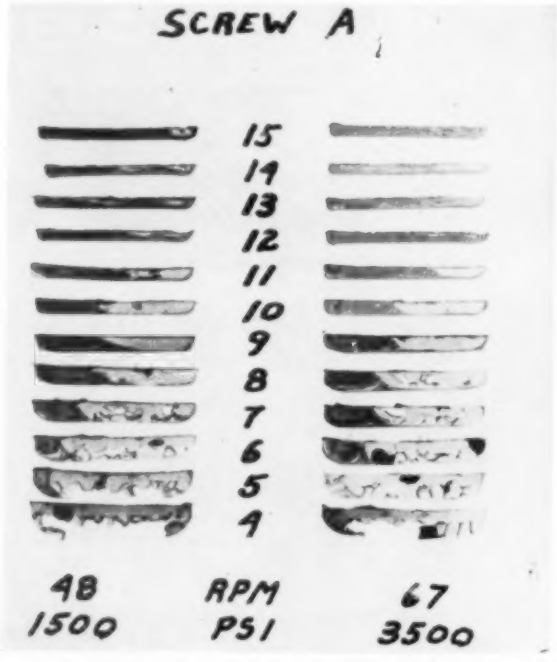

Figure 13. Effect of pressure at constant output rate.

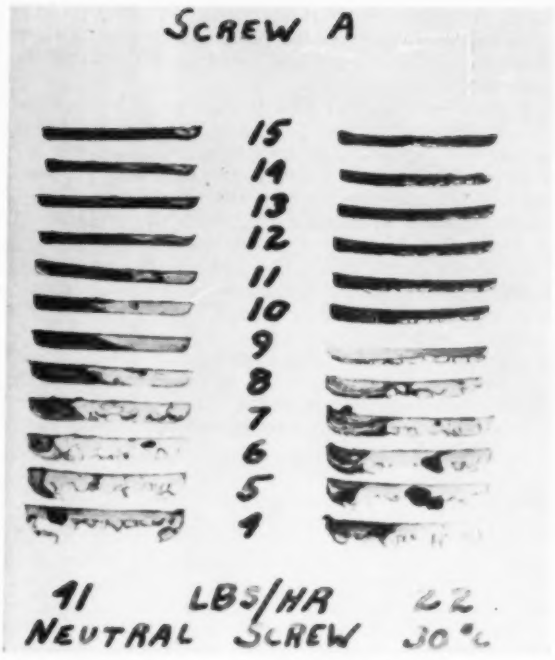

Figure 14. Effect of screw cooling at constant screw speed.

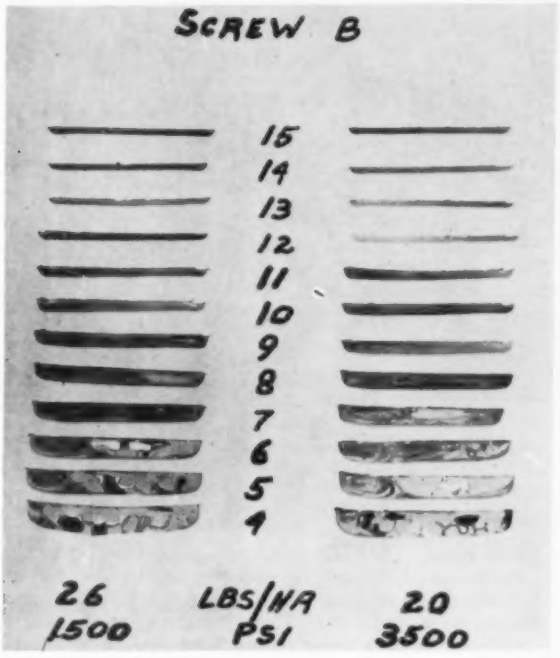

Figure 15. Screw B—Effect of pressure at constant screw speed.

later, blended material passes over it, becoming well mixed well back in the screw. The effective channel depth has thus been reduced as a result of the frozen or slowly moving layer on the screw. This increases the effective rate of shear or mixing intensity and lowers the discharge rate. Raising the screw speed to 96 rpm, the maximum for the machine, as in the bottom sample of Fig. 8, brought the rate to only 83% of the rate with a neutral screw. The volume of well-mixed material in the channel was again reduced, but the good quality of the extruded product was maintained.

Extreme hang-up is noted on the ends of the cooled screw samples with the resultant white streak in the core of extrudate. This points up an inherent weakness in design which can be overcome by proper contouring of the end of the screw. A conical end having an included angle of about 120° will eliminate this hangup area.

Fig. 9 shows a comparison between neutral and cooled screw operation at 48 rpm, 1500 psi pressure, where a larger quantity (12 lbs.) of the color blend was extruded after starting with the uncolored material. The extreme hang-up is still noted on the end of the cooled screw, although the white material has been displaced from the screw surface.

Polyethylene Extrusion

Essentially identical behavior was found in extrusion of polyethylene. Fig. 10 shows the effect of pressure with a neutral screw at 48 rpm. It was not possible with polyethylene to remove the plugs from the adaptor and valve sections without destroying their shape; thus the specimens shown are the screw helices only. The samples are wrapped around fluorescent lighting tubes for internal illumination. The light areas in the forward end of the screw (left hand side of picture) are external shrinkage pockets caused by release from the barrel during cooling and do not represent areas of poor mixing. These were present to a very minor degree in some of the vinyl samples.

The effect of screw cooling at 48 rpm and 1500 psi pressure is shown in Fig. 11. This is also seen to be similar to the results obtained with the vinyl compound.

Circulating Flow in Channel

Thin sections cut from each turn of polyethylene helices in a plane through the axis of the screw are shown in Fig. 12. These illustrate the effect of pressure at a fixed screw speed of 48 rpm, corresponding to the conditions of Fig. 10. Samples numbered 15 are from the last turn at the exit end. Normally the material in turns 1 and 2, at the feed hopper, are completely unfluxed and that in the 3rd turn not sufficiently fluxed to permit sectioning in this manner. The left hand side of the specimens are from the rear portion of the channel adjacent to the leading edge of the advancing flight.

The build-up of mixed material in the rear portion of the channel with progression through the screw and the circulating flow in this area are clearly indicated. Earlier fluxing and more complete mixing at the exit end are apparent in the higher pressure samples on the right.

Raising the screw speed to 67 rpm at the higher pressure to return to the 1500 psi rate of 41 lbs./hr., produced the effect shown on the right hand side of Fig. 13. The fluxing was delayed, the inventory of well mixed material was reduced, but the final degree of mixing is still better than at the lower pressure. Figs. 12 and 13 represent conditions similar to those shown for the vinyl compound in Fig. 7.

The effect of screw cooling at 48 rpm and 1500 psi pressure is shown in Fig. 14 in comparison with a neutral screw. These correspond to the conditions of Fig. 11. Good mixing is ultimately achieved with the

TABLE I

2.0" Diameter Screws

Screw Type	B Metering	Metering Nylon Type*	Decreasing Pitch
Pitch at feed, in.	2.0	2.0	2.9
Pitch at discharge, in.	2.0	2.0	0.75
Depth at feed, in.	0.370	0.375	0.33
Depth at discharge, in.	0.062	0.095	0.38
Compression Ratio	5.4	3.4	4.0

* Constant depth from feed to metering section.

cooled screw, but unfluxed pellets can be observed adhering to the screw surface all the way to the exit end.

Other Screw Types

Three additional 2.0 in. diameter screws, having the dimensions shown in Table I, were evaluated with polyethylene under the neutral condition at 48 rpm.

Channel sections from screw B are shown in Fig. 15. This screw is similar to screw A except for a smaller channel depth in the metering section. Comparing Fig. 15 with Fig. 12, it is seen that the smaller channel depth results in better mixing, even at the lower pressure, but that the general fluxing and circulating flow mechanisms are essentially the same for the two screws.

In Fig. 16 it is observed that little mixing took place in the nylon type screw, C, at the lower pressure. Raising the pressure to 3500 psi caused a back-flow effect which over-rode the metering section to produce considerable mixing in the last few turns of the feed section. Similar effects are noted in Fig. 17 for the decreasing pitch type screw, D.

Careful examination of Figs. 12 through 17 reveals two circulating paths in some of the deeper channel areas. One appears to be a closed path in the rear portion of the channel. Actually this is probably a helix advancing in a direction outward from the plane of the specimen. In some cases, particularly noticeable in Figs. 16 and 17, a portion of the mixed material is carried completely across the channel along the screw surface, by-passing the unfluxed material, until it meets the trailing edge of the forward flight where it rises to again be carried in a thin layer across the surface of the barrel. This is also visualized as a helical path but advancing at a more rapid rate than the circulating path in the rear portion of the channel. Both of these helical, circulating flow patterns should contribute to the degree of mixing.

Effect of Starve Feeding

The effect of starve feeding is illustrated in Fig. 18. Here the top sample again represents the normal condition with a neutral screw at 48 rpm. Without changing any machine conditions, the feed was then metered into the hopper at a rate equal to one-half of the normal delivery rate. This resulted in a reduction in material inventory to about 4½ turns at the exit end as shown in the center sample. The degree of mixing was improved, however, as a result of the increase in residence time in the metering section at the lower rate of throughput.

Carrying this a step further, the screw speed was then doubled, to 96 rpm, while still maintaining the reduced feed rate of 29 lbs./hr. This resulted in a further reduction in inventory, as shown in the bottom sample of Fig. 18, and further improvement in mixing.

Figure 16. Screw C—Effect of pressure at constant screw speed.

Figure 17. Screw D—Effect of pressure at constant screw speed.

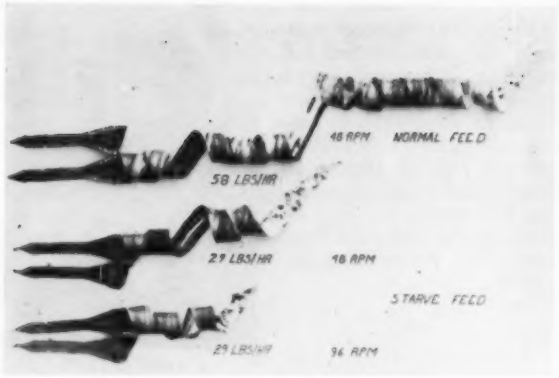

Figure 18. Effect of starve feeding.

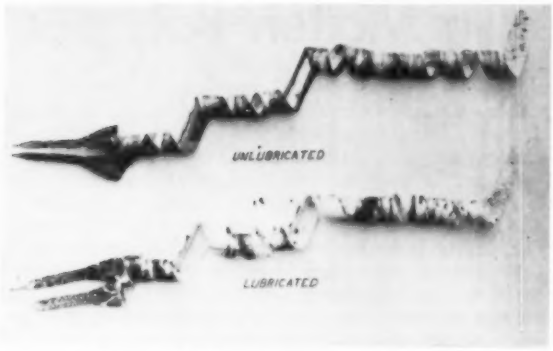

Figure 19. Effect of excessive lubricant.

The improved mixing is attributed, in this case, to the increase in rate of shear at the higher screw speed. These results confirm earlier conclusions that the degree of mixing accomplished in the screw is directly related to the product of the shear rate and the residence time in the area in which the shearing takes place.

The theoretical pumping capacity of the metering section under both of the starved feed conditions was considerably greater than the actual delivery as determined by the feed rate. Complete emptying of the screw was prevented by the die restriction and the resultant pressure build-up. Other experiments have shown that by further restriction at the die or valve, the fluxing point could be moved backward, at the reduced feed rate, until the screw was again completely filled. This would require a pressure of about 4000 psi at the 48 rpm condition.

Effect of Lubricants

The screw removal technique provides a useful method for study of factors such as lubricity in vinyl compounds. This is the subject of another investigation by the present author and will not be discussed in detail in this paper. An example of excessive lubricity is shown in Fig. 19. It is noted that the material friction against the barrel and the screw surface has been reduced to the point that essentially no mixing takes place. There is some smearing of the brown material along the barrel surface but this material is not carried down into the channel by the advancing flight and there is no circulating flow in the rear portion of the channel such as that previously shown for polyethylene

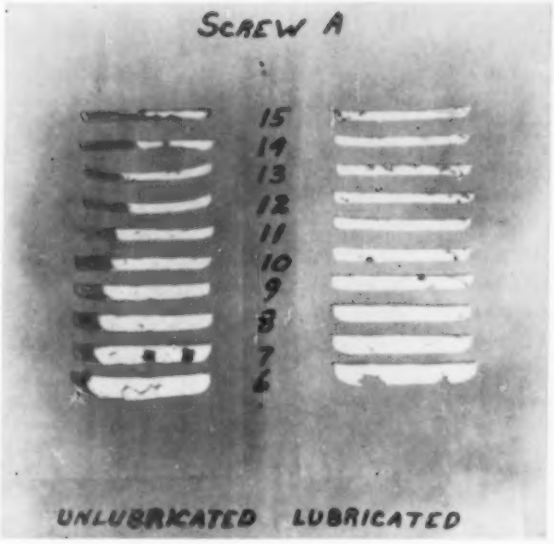

Figure 20. Effect of excessive lubricant on mixing and circulating flow.

and less highly lubricated vinyl compounds. Channel sections illustrating this complete lack of circulating flow are shown in Fig. 20 in comparison with a conventional vinyl compound containing less lubricant.

Excessive lubricity also manifests itself by delayed fluxing and marked reductions in frictional heat, stock temperature and output rate, in addition to the impairment in mixing and product quality.

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J. Kenneth Lund

Chain Rupture by Shear in Molten Polymer

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Abstract

Polyisobutylene of a wide range of molecular weights was subjected to intense mechanical shear at varied temperatures. The force time curves in the capillary shear apparatus and the solution viscosities were determined. The fractional molecular weight drop increases as the temperature is lowered, as the initial molecular weight is increased, or as the shear rate is increased. In contrast, the specific rate of bond rupture among chains is only slightly dependent upon the molecular weight at low shear rates, but is independent of molecular weight at high shear rates. The results fit the empirical relation:

$$b = K \cdot e^{11,000/RT} \cdot \gamma^{4/3}$$

where

b = specific rate of bond rupture, mol fraction bonds ruptured per second
K = constant
R = gas constant
T = absolute temperature
Υ = shear rate, seconds^{-1}

As in the case of polymer solutions, continued shear produces molecular breakdown at a gradual decelerating rate. The chains become reduced to lengths which can relax without rupture when shear is continued.

* The research reported here was sponsored jointly by the Army and Navy under Signal Corps Contract No. DA-36-039SC-70154; O.N.R. 356-375.

THIS PAPER represents a study of the degradation of a polymer melt by mechanical action. Its object is to determine the effect of experimental variables such as shear rate, temperature, and initial molecular weight on the rupture of polymer chain bonds during shearing action.

The overall effect of degradation is to alter the polymer structure, drastically reduce the average chain length, and cause a deterioration of almost all of the polymer's worthwhile properties.

The mechanisms of degradation are many. Their causes are well understood in some cases and can be minimized. However, they can not be completely eliminated. A better understanding of the cause and effect of polymer degradation can be obtained only through continued study of the chemical and process techniques used in their production.

The most commonly recognized causes of polymer degradation are (1) heat, (2) attack by oxygen, (3) attack by acids and alkalis, (4) radiation, (5) ultrasonics, (6) photodegradation, and (7) mechanical action.

Common mechanical means of producing degradation are grinding, milling, shaking, shearing, beating and high speed stirring. Many of these take place during polymer processing. Up to the present time, little evidence has been published indicating the effect of process conditions on the extent of degradation by these means.

There has been a considerable amount of work done on the degradation of polymer solutions by shearing action (Refs. 1-15). The work has been stimulated by the need for improving polymer additives in lubricating oils. These additives are used to improve the viscosity and viscosity-temperature coefficient of these oils. Although quite satisfactory at the beginning of their use, most polymer blended oils drop in viscosity as they are used and eventually lose much of the advantage gained by adding the polymer.

The study of polymer solutions affected by shear has been more complete than on polymer melts.

Aside from qualitative discussions of the occurrence of molecular breakdown in polymer melts, comparatively little work is described in the literature. The process of shearing polymer melts has been used to produce

block and graft copolymers (Refs. 16, 17, 18, 19, 20).

The thermodynamics of heat generation during the shear of polymer melts has been the subject of some study (Refs. 21, 22). Baramboim has reported on the degradation of polymers during grinding operations (Ref. 23). He reported finding a limiting molecular weight, $M\infty$ in grinding the polymers polyvinyl acetate, polymethyl methacrylate, and polystyrene in air. The decrease of molecular weight, M, followed the expression

$$M = (M_o - M\infty)e^{-kt} + M\infty$$

where

M_o = initial molecular weight
k = constant
t = time of grinding

Mechanical Shear Degradation—Theory

When a polymer system is subjected to a shearing force, it is necessary to consider the polymer chain configurations in the melt and the mechanisms by which the chains flow.

The commonly accepted picture of polymer chain configuration is as follows (Ref. 24). In an amorphous linear polymer, each long chain assumes a random configuration. The chains are closely packed, so that many segments of different chains can be found in the same volume element of the polymer. Neighboring chains overlap and are intimately associated with each other.

With the application of a shear force to a polymer system, deformation occurs simultaneously by the following mechanisms. The first is a small elastic deformation which quickly reaches an equilibrium value. This is caused by the bending and stretching of primary and secondary bonds. Further distortion affects the polymer in the following manner. The long chain molecules are in close contact with each other at entanglement points. However, these points are not permanent and the chains slip out of them with continuing deformation. During this period, the second and third mechanisms take place. The second is a time dependent elastic deformation and the third is an unrecoverable viscous flow. The former represents chain uncoiling and the latter is the slipping of polymer chains past one another.

A great deal of intensive work has been done over the past few decades to develop theories explaining the flow of liquids.

Eyring (Ref. 25) visualizes the elementary flow process as the jump of a molecule from one equilibrium position to another. This theory is helpful in describing the flow of simple liquids. However, modifications of Eyring's ideas are necessary for long chain molecular flow.

It was later suggested by Ewell (Ref. 26) that in the polymer case, the elementary process for viscous flow consists of the displacement of only a small segment of the molecule and not the displacement of the entire molecule as a unit.

The segmental flow mechanism is not adequate in itself to explain the high viscosities of the very long chain molecules. The segments of a long chain are not completely independent and must move together if the chain as a whole is to progress. This is due to the inter and intra chain connections of the polymer segments. A segment is connected to other segments of its own chain (intrachain) by primary valence bonds and to segments of other chains (interchain) by secondary bonds and entanglements.

The more complicated the configuration of the molecular system, the more difficult is the attempt to unravel the mechanisms by which it flows. All of the answers are not before us, but enough is known to enable us to have a reasonable understanding of the manner in which a polymer system reacts to an applied shear force.

When this force is applied, the deformation and flow of simple liquids can be imagined as the movement of one layer of molecules past another with a greater velocity in the direction of shear. However, it is difficult to imagine the relative movement of polymer layers taking place in a polymer system because of the intimate contact and enmeshment between chains. As in any liquid, there is a velocity gradient in a direction perpendicular to that of the applied shear force. Chain segments and entanglement points in the velocity gradient plane move past one another as the system deforms under shear. It is quite possible for one end of a chain segment to be moving temporarily with a greater velocity than the other end. Consequently, the segment will be stretched and, assuming that it connects two entanglement points, will be forced to disentangle and assume a new configuration.

The stretching of molecular segments can have no damaging effect on the chain unless one or more of the main chain bonds are broken. The application of

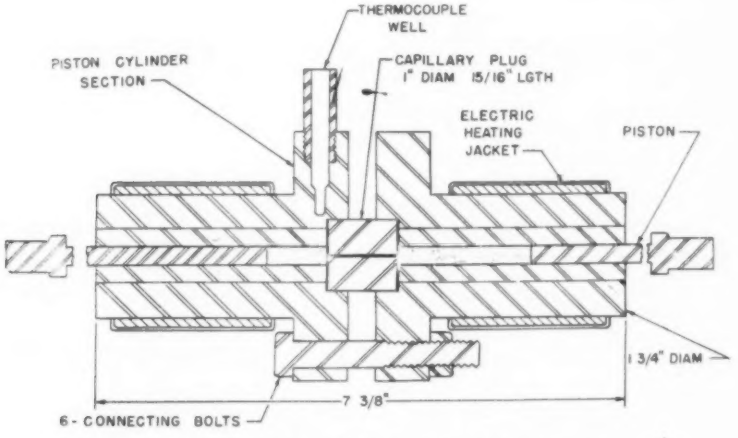

Figure 1. Shear section of the experimental apparatus.

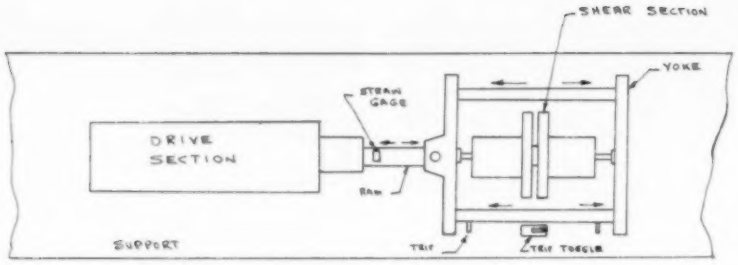

Figure 2. Experimental apparatus.

severe shear forces to a polymer system in a period of time which does not allow the chain segments to disentangle could conceivably bring about rupture of a main chain bond.

The ability of a chain segment to deform is directly related to the relaxation time for this mechanism. This relaxation time will be dependent on several factors. They are (1) the effective crossectional area of the polymer chain, (2) the chain roughness, (3) the number of entanglements that the remainder of the chain is involved in, and (4) the degree of segmental coiling between entanglements.

The effective crossectional area of the polymer chain is related to the molecular weight of the repeating monomer unit. One would expect a chain of high molecular weight per monomer unit to respond to an applied shear force less quickly than one of low molecular weight.

Chain roughness describes the presence of substituent groups or side chains which jut out from the main chain at dispersed points and considerably slow the deformation process when they reach an entanglement point.

The third factor takes into account the entanglements of the remainder of the polymer's chain segments. A segment is not free to disentangle by itself. When it begins to slip out of an entanglement point, a neighboring segment of the same chain is put in tension. This tension is transmitted down the chain and succeeding segments react by stretching and attempting to slip out of their entanglement points. The result is that a segment can move only as far as the rest of the chain permits it to.

The fourth factor describes the degree of coiling of the chain segments. If, in the same chain, a segment adjacent to one under tension and attached to it through an entanglement point is in a completely uncoiled state (at its limit of elastic response), it will generally exert more resistance to the flow of the adjacent segment than if it were in a more coiled configuration.

In a model of polymer chain flow we may picture the various chains, when subject to no shearing forces, to be considerably intermingled. Thermodynamically, the chain segments of the various chains are much alike and no very strong signal goes out to any one chain segment reminding it that it is a particular member only of chain i. As a shearing motion is begun, then the mixed up chain segments are reminded by occasional tugs that they are linked to chain i. Similarly for chains k, l, m, etc. As shearing motion is continued, there is observed to arise a selectivity of domain for the segments of chain i, etc. They are more often to be found in the neighborhood of each other than before. In the limit, one would say that the individual chains tend to 'ball up', for i segments to stay with i segments. The interpenetration, and therefore the drag of neighboring chains on each other will decrease with increasing shear rate.

As a not too exact analogy, we may consider two endless gypsy caravans on a road. At rest, there will be considerable intermingling. Start-up will be difficult. As each caravan begins to move slowly, one will tend to line up and stream along one side of the road, the other on the other side. As speed increases intermingling decreases sharply, until at high speed there will be practically none. The permanent loss of a member from one band may be considered as loosely analogous to the breakdown of a polymer molecule. The loss will be low in rate at low speeds for the 'forces' will not be high. The loss will be higher at high speed. In all cases, the loss will be proportional to the time of shear, at constant velocity of shear. However, in the initial alignment process we might expect an abnormally high fatality rate as the de-segregation has not reached its ultimate. To sum up, we would expect from this model that the viscosity of polymer melts will drop with increasing shear rate; that at a constant shear rate the molecular degradation in a given size range will be proportional to their numbers and to the time of shear, and will be more severe at high shear rates. In any case, the rate of breakdown will be milder than one would expect for the case of completely interpenetrating-chains because of the 'balling up' of the large molecules.

This argument, extended to very high shear rates on polymer melts, predicts that larger and larger segments of polymer chains will agglomerate and 'ball up' to cause still further relief of internal stresses. This will result in macroscopic 'crumb' flow or 'melt fracture' (Ref. 27) where lumps of polymer roll over each other.

It is helpful to compare the above considerations of polymer melts with that for dilute solutions of polymers. For polymer molecules in dilute solution it may readily be shown that the maximum force tending to produce bond rupture, $F_{max.}$, on a chain molecule is: (Ref. 12)

$$F_{max} = \frac{3\pi M^2 \eta_i \Upsilon a L}{8 m^2}$$

where

M = molecular weight of the (homogeneous) polymer chain
m = molecular weight of the monomer unit
η_i = solution viscosity
Υ = shear rate
a = effective radius of monomer unit, considered as a sphere
L = distance between monomer centers

This equation may be put in a form more useful to the plastics engineer:

$$B = \eta_i \Upsilon M_w^2 = F_{max} \frac{m^2}{k a L}$$

= breakdown index

and k is a factor of the order of unity for polymer homogeneous in molecular weight and about 10 for crude polymer (i.e. almost all commercially available polymers).

Since the force to break a bond is generally that for breaking a carbon-carbon bond, and since the factor $a \cdot L$ is essentially constant for most commercially available polymers, it turns out that B_{lim}, the calculated limit of B before chain rupture, is reasonably constant, and has a magnitude of about 1.4×10^{14} to 3.1×10^{14} in c.g.s. units.

The usefulness of the simple equation

$$B = M^2 \eta_1 \Upsilon$$

stems from the fact that it appears to afford a quick guide to polymer breakdown. As shown by Pohl (Ref. 12) breakdown in solution does not seem to occur unless $B \leqq B_{lim}$ in the several experimental cases examined. The theory further indicates that variation in chemical structure is not a very important factor insofar as stability to shear forces is concerned. On the other hand, the molecular weight, the molecular weight distribution, the chemical reactivity, and geometric factors such as branching or crosslinking are factors relatively more important.

Extension of the theory to rate equations still leaves the expectation that molecular weight will play a prominent role in solutions of polymers. This is to be contrasted with the expectation that at high shear rates polymer melts will experience chain rupture relatively independent of the molecular weight (at constant melt viscosity).

Since flow process for chains is difficult to analyze theoretically, the experimental approach will be of considerable help in understanding it.

The influence of shear rate, temperature, and initial chain length were experimentally investigated and the results are presented to give an indication of their effect on the degradation of a linear, non-polar, amorphous polymer by shearing action.

Experimental Work

Polyisobutylene samples of three different molecular weights were used in this investigation. All were manufactured by the Enjay Company, Inc., under the trade name of Vistanex resins. The viscosity-average molecular weights reported for these samples are 51,300, 1,020,000 and 5,250,000. A wide range of weights was chosen so that the effect of initial molecular weight on degradation could be studied.

In order to subject the polymer samples to shearing action, apparatus was designed and built to do this by forcing the sample through a small capillary. The polymer was sheared in the capillary and the force necessary to produce this flow through the capillary was measured by suitable strain gage equipment.

The capillary was contained in the shear section of the experimental apparatus. A sectionalized drawing of the shear section is shown in Fig. 1. The pistons shown in this figure were alternately driven into the cylinder at a constant rate of speed. Polymer in the cylinders was forced back and forth through a capillary hole located in a steel plug section in the center. Electric heating jackets supplied heat to maintain the shear section at the desired temperature. The temperature was observed by use of a thermocouple placed in the thermocouple well.

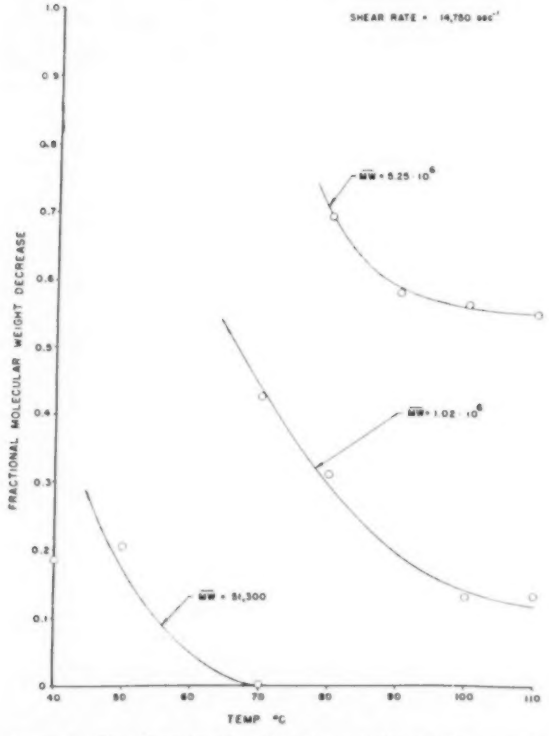
SHEAR RATE = 14,780 sec⁻¹
$\overline{MW}$ = 5.25 · 10⁶
$\overline{MW}$ = 1.02 · 10⁶
$\overline{MW}$ = 51,300
FRACTIONAL MOLECULAR WEIGHT DECREASE
TEMP °C

Figure 3. The fractional molecular weight of the experimental samples as a function of temperature in the 40° to 110°C range.

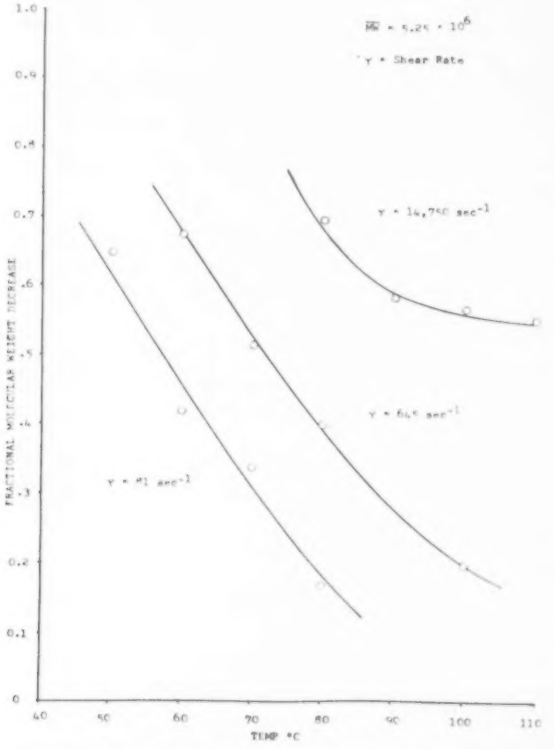

Figure 4. The fractional molecular weight decrease of polyisobutylene as a function of temperature and shear rate.

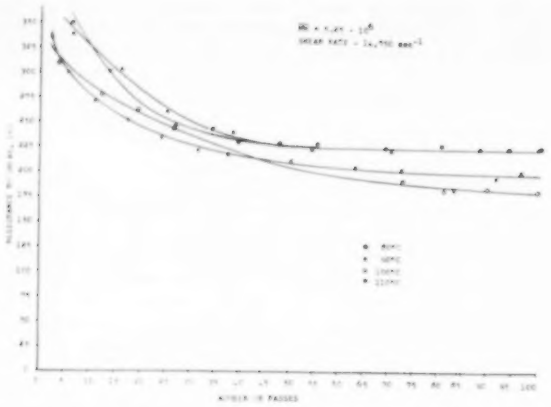

Figure 5. The force required to move a polymer sample through a capillary as a function of the number of passes, or total capillary residence time.

The force required to drive the pistons into the cylinders was supplied by the drive section which was connected to the shear section by a yoke. This arrangement is shown in Fig. 2. The drive section was a linear actuator which moved at a constant rate of speed. Its direction of motion was reversed very rapidly by hitting a trip switch when a piston had been driven completely into its cylinder. In this manner, the shearing action was automatically continued until a run was completed.

A strain gage was located on the ram of the drive section and the force required to drive a piston into its cylinder was measured. This force was directly related to that required to move the polymer melt through the capillary.

Polymer samples were forced through the capillary for 100 passes at different temperatures and shear rates. The shear rates determined in this paper are those which were calculated to exist at the wall of the capillary. They are determined by the following relationship (Ref. 28).

$$\Upsilon = \frac{4Q}{\pi r^3} \quad \text{where} \quad \begin{array}{l} \Upsilon = \text{shear rate} \\ Q = \text{volumetric rate of flow} \\ r = \text{radius of capillary} \end{array} \qquad \text{(Eq. 1)}$$

The linear speed of the pistons was constant. Therefore, the radius of the capillary was changed to vary the shear rate. Three different capillary sizes were used, which gave calculated shear rates of 81, 645 and 14,750 sec^{-1}.

The amount of degradation produced in this apparatus was determined by comparison of the molecular weights of the samples before and after shearing. The viscosity-average molecular weights of the samples were determined in the following manner. Relative viscosities of polyisobutylene-incyclohexane solutions were measured and intrinsic viscosities were determined by extrapolation of $\frac{\ln \eta_r}{c}$ (η_r = relative viscosity; c = concentration) to zero concentration (Ref. 29). The molecular weight of the sample is related to the intrinsic viscosity $[\eta]$ by the following relationship (Ref. 30).

$$[\eta] = KM^a \qquad \text{(Eq. 2)}$$

Results

The fractional molecular weight decrease of the experimental samples as a function of temperature in the 40 to 110°C range is plotted in Fig. 3. These samples were of differing initial molecular weight (51,300 to 5,250,000) and each was subjected to a shear rate of 14,750 sec^{-1}.

Several observations can be made. Degradation appears to be very dependent on temperature in the lower range of temperatures at which each sample was sheared. And, at its upper limit, temperature appears to have lost a great deal of its influence on the extent of degradation.

The first observation seems to be indicative of the increasing difficulty of the chain segments to disentangle themselves. Their thermal motion is being reduced and consequently the relaxation time of the disentangling mechanism is lengthening. It was not possible with the experimental apparatus used, to determine if the sharp increase in degradation at lower temperatures was approaching complete breakdown of the polymer at some one temperature for each sample concerned, or if the curves were leveling out and would assume a different shape. (It is considered unlikely that the former would occur.)

In Fig. 3, the experimental values show that at any one temperature, the higher the initial molecular weight, the greater is the degradation. This also holds true for data collected at other shear rates. It is natural to expect that samples of higher molecular weight will be more seriously affected because the number of chain segments per molecule of these longer molecules involved in entanglements is greater than that of the shorter chains. Further, to attain a certain set degree of degradation, one must go to lower and lower temperatures to obtain this value on using shorter polymer chain samples. This is probably attributable to the greater overall mobility of the shorter polymer chains. In order to reduce this mobility to a level at which one can produce the desired degradation, the thermal motion of the molecules must be reduced.

Fig. 4 is a plot of the fractional molecular weight decrease of polyisobutylene (MW_n = 5,250,000—sheared for 100 passes) as a function of temperature and shear rate. As the shear rate is increased at constant temperature, the degradation increases. However, the influence of shear rate appears to decrease as the rate is increased. For example, at 80°C, as the shear rate is increased from 81 sec^{-1} to 645 sec^{-1}, a factor of 8, the degradation is doubled. But, on increasing the shear rate from 645 to 14,750 sec^{-1}, a factor of 23, the degradation is increased by only a factor of 1.7. This trend is somewhat misleading because, as it is shown later, the rate of bond rupture is proportional to the shear rate, to the 1.30 power. The data plotted in Figs. 3 and 4 are the results of shearing polymer samples through a capillary for 100 passes. As the shear rate is increased, the total capillary residence time decreases. A molecule sheared at a rate of 14,750 sec^{-1}, is experiencing shear for a total of 1.08 seconds for 100 passes, whereas a shear rate of 81 sec^{-1} gives the molecule a total of 75.2 seconds in the capillary. Therefore, the extent of degradation shown in these figures is not compared on the basis of equal time under shear in the capillary. A plot of the degradation as a function of these same variables but at equal capillary residence times will show that the influence of shear rate on the degradation increases as the rate is increased.

The influence of shear rate conditions on the degradation of these samples, as shown by these data, is in-

dicative of the effect of applying shear forces to the polymer system in a time period which does not allow the chain segments to disentangle before rupture of a bond.

The force required to move a polymer sample through the capillary was observed as a function of the number of passes, or total capillary residence time. An example of this data is plotted in Fig. 5 for samples of initial molecular weight, $5.25.10^6$, at a shear rate of 14,750 sec^{-1} at different temperatures. This force is high initially and then drops off sharply with time and finally appears to approach a constant value.

Polymer viscosity is directly related to this force and is also directly related to the molecular weight of the sample. Consequently, the change of this flow force with time at a constant shear rate is indicative of the change of the polymer molecular weight with time.

Apparently, either most of the chain rupture or adjustment to flow occurs within a short time after the polymer is subjected to shear. The leveling out of the shear resistance indicates either that degradation has essentially stopped or that adjustment to flow is nearly complete, probably the former. The long chains have been reduced in size to lengths that have the mobility to disengage from any point of entanglement under the shear rate condition applied. This is directly analogous to the change of molecular weight of polymer samples in solution with time (Refs. 1-15).

According to Fig 5, there is no overall clearcut distinction between force-time data collected at different temperatures. It is expected that a greater resistance would be encountered at lower temperatures because of increasing polymer viscosity. The limitations of the force measuring apparatus and the apparatus drag at different temperatures combined to produce a picture of the progress of degradation which is slightly out of focus, at best. It is hoped that further refinements of the experimental apparatus and collection of data will present a clearer picture.

Rate of Degradation

All polymer samples were forced through the capillary for 100 passes. This resulted in different total capillary residence times, depending on the shear rate applied. It is not completely justifiable to assume that the rate of degradation is constant over the entire time period for each shear rate studied. However, for the sake of estimating the effect of shear rate, temperature, and initial molecular weight, the degradation is averaged over the total capillary residence time to determine an "average" rate of degradation.

In order to consider the damage done to a polymer chain, regardless of the molecular weight, the mole fraction of bonds ruptured was determined. This quantity, in terms of the polymer *DP* (Degree of Polymerization), is expressed by the following relationship.

$$\text{Mole Fraction Bonds Broken} = \frac{1}{2}\left[\frac{1}{DP} - \frac{1}{DP_o}\right] \quad \text{(Eq. 3)}$$

where *DP* is the degree of polymerization of the degraded polymer and DP_o is the degree of polymerization of the initial polymer sample.

The mole fraction of bonds ruptured, averaged over the total capillary residence time for each sample, is the average rate of bond breaking *b*, which is used in this paper.

Log *b* was plotted vs. $1/T°K$ because the thermal influence on *b* was expected to be closely related to the polymer viscosity. This plot is shown in Fig. 6. There appears to be a linear dependence of log *b* on $1/T°K$. And, although there is an indication of a slight dependence of *b* on the initial molecular weight of the samples at lower shear rates, it is not too pronounced. At the highest shear rate used, 14,750 sec^{-1}, *b* appears to be independent of the initial molecular weight of the polymer. This does not seem unlikely when it is considered that, at higher shear rates, there is only time enough for a chain segment and its nearest neighbors to respond to an applied shear force.

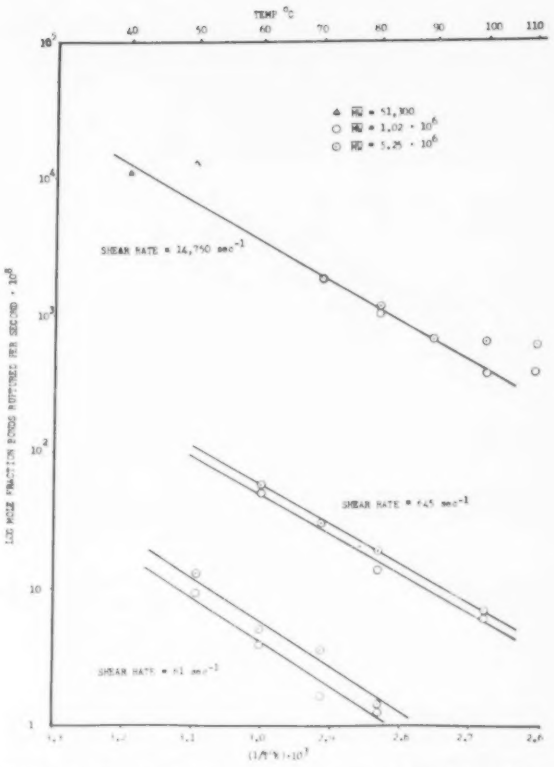

Figure 6. The log of the average rate of bond breaking vs. $1/T°K$.

Log *b* is also plotted as a function of log shear rate in Fig. 7, at different constant temperatures. These curves are plotted as a mean of the curves shown on Fig. 6 at different shear rates. The average slope of these lines is 1.30, with very little deviation from this mean.

The plot on Fig. 6 is represented analytically by the following relationship.

$$b = e^{k'} \cdot e^{11,000/RT} \cdot \gamma^{1.30} \quad \text{(Eq. 4)}$$

The relationship gives the dependence of the rate of bond breaking *b*, on temperature and shear rate. R is the gas constant and k′ is a plot constant.

The initial molecular weight does not appear explicitly as a term in Eq. 4. As discussed above, although a trend is indicated at lower shear rates, no definite conclusion can be drawn from these data.

However, if the trend shown accurately reflects the influence of initial molecular weight, then the following effect would be noted in Eq. 4 and in Fig. 7. At a constant temperature, log *b* plotted at different shear

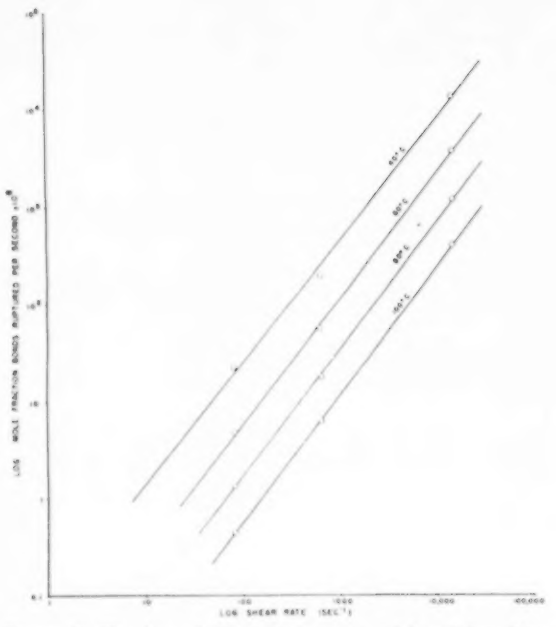

Figure 7. The log of the average rate of bond breaking as a function of log shear rate.

rates as a function of initial molecular weight would result in lines of varying slopes, at lower shear rates. The lower the initial molecular weight, the greater the slope of the plotted data. But, these curves would converge at higher shear rates to form a single curve which would be consistant with the argument presented previously. Consequently, the exponent of the shear rate term and the equation constant ($e^{K'}$) would be dependent on the initial molecular weight. Further work will be required to establish this relationship.

Consideration of the results shown by these data and of the mechanisms by which they occur suggest the following hypothesis.

The rate b, of bond rutpure becomes independent of initial molecular weight, above a minimum molecular weight range, as the polymer melt is subjected to greater rates of shearing.

Conclusions

1. The fractional molecular weight decrease ($\Delta MW/MW_o$) of a polyisobutylene melt due to shearing action increases as:
   a. the temperature is lowered
   b. the initial molecular weight is increased
   c. the shear rate is increased

2. Much of the polymer degradation takes place when the polymer is first subjected to shearing action. Thereafter, bond rupture decreases in rate. The chains become reduced to lengths which can relax without rupturing when further shear force (equal to the original) is applied.

3. The rate of bond breaking (mole fraction bonds ruptured per second) b, is dependent on shear rate Υ, and temperature T, and is estimated by the following relationship,

$$b = K \cdot e^{11,000/RT} \cdot \Upsilon^{1.30}$$

where K and R are constants.

4. Collected data suggest the following hypothesis: The rate b, of bond rupture becomes independent of initial molecular weight, above a minimum molecular weight range, as the polymer melt is subjected to greater rates of shearing.

5. At lower shear rates, there is an indication of the dependence of rate of degradation on the initial molecular weight, but it is not pronounced enough to determine with precision at the present time.

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John B. Howard

A Review of Stress-Cracking in Polyethylene

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THE FACT that low molecular weight polymers of ethylene could be made to rupture by contact with "mobile polar nonsolvents" was disclosed by Richards in a paper on the solubility and swelling of these polymers in 1946 (Ref. 1). Little notice was taken of this information for some time until growing utilization of polyethylene for cable sheath and for flexible containers brought to light the devastating effects of soaps and detergents on certain polyethylenes of moderately high molecular weight (i.e. melt index $\cong 2$) under stress. In 1950 Hopkins, Baker, and the present author (Ref. 2) reported marked differences in the strength of certain polyethylenes under polyaxial as opposed to uniaxial stress and related this to the stress-cracking behavior of these polymers. Shortly thereafter Carey (Ref. 3) and Richards (Ref. 4) presented additional findings and DeCoste, Malm, and Wallder (Ref. 5) reported the results of a study of cable sheath failures, introducing the bent-strip test which, in spite of its apparent shortcomings, remains the most widely used procedure for assessing environmental stress-crack behavior. Of the publications which have followed, some have reported data using this test, others have proposed test procedures specific to certain approaches and still others have suggested different applications, to the general problem of testing polyethylene as a material apart from end-use considerations. These will be considered later, following a review of the present state of knoweldge of the phenomenon itself.

Recognition and Characterization of Environmental Stress-Cracking

A. Distinction From Other Types of Stress-cracking

Polyethylenes can be subject to rupture under a variety of circumstances all of which are literally "stress-cracking." Failure under impact, for example, at either ordinary or very low temperatures can qualify under the broadest interpretation of the word, but by common agreement, the term is usually reserved for those cases where failure does not occur immediately on imposition of stress but only after some finite interval. The usage of the last ten years has further restricted application of the term insofar as polyethylene is concerned to circumstances which involve the presence of an external sensitizing or accelerating agent as opposed to fatigue failures in the absence of such media. Failure of the latter type could perhaps be considered an extension of thermal embrittlement, or thermal stress-cracking as it is possibly better called, and the presence of a sensitizing environment could be viewed as merely a means of inducing the same sort of failure at lower stresses and/or shorter times. In other words, the three superficially different phenomena could be thought of as basically related. All three are in many ways reminiscent of stress corrosion cracking in metals (Refs. 6, 7) and of stress rupture in glass, (Ref. 8) and may sometimes be difficult to distinguish from each other in polyethylene.

When a specimen or part fabricated from polyethylene and maintained under constant external stress (external to the material but not necessarily to the part) is at one moment intact and at a subsequent moment ruptured, it is evident that one of two things has happened. Either the polymer has been weakened by the action of some agency, operating externally or internally, to an extent such that the material can no longer sustain the stress imposed upon it, or a physical change of some sort within the polymer mass has brought about a redistribution of the internal stresses present to produce, in combination with externally applied forces, a resultant exceeding the strength of the material at the point of failure. The agency operating in the first instance may be either chemical or physical in nature. The former most probably involves oxidation, since pyrolytic breakdown is very unlikely in the temperature range at which polyethylenes remain solid, while

the latter has to do with details of the contact between the polymer and its environment. The second possibility presumably involves purely physical changes within the polymer mass: modification of the amount and/or nature of the crystalline phase of the material, or to use other phraseology (Ref. 9), changes in the crystalline texture of the polymer.

There are thus three different agencies (physical interaction of the polymer with its environment, modification of its crystalline phase, and oxidation) which apparently are capable of initiating superficially similar failures in polyethylene. This has led to confusion and sometimes to the mistaken imputation of failures caused by one to another of the three. Unless experiments are carefully designed, distinction is not always easy. When, for instance, rupture is observed in a specimen of polyethylene under stress in an oven at 100°C, is the failure to be ascribed to thermal stress-cracking or to oxidation? Or in a similar specimen under stress in an open container of water at 90°C, is the failure environmental, thermal or oxidative?

To cite a specific case by way of illustration, data have been obtained for an ASTM Type III polyethylene extruded without addition of stabilizer to a wall thickness of 0.014" on #20 AWG copper wire. This polymer was a coordination catalyst product whose reduced specific viscosity (RSV) at 0.5000 g./100 ml. in tetrahydronaphthalene at 120 ± 0.02°C was 3.14. Test specimens (Fig. 1) were prepared by wrapping the insulated conductor tightly around itself for ten turns to give small helices whose outer surfaces were under approximately 50% strain, as has been done in earlier work (Refs. 10, 11, 12). Such specimens were subjected to a temperature of 100 ± 1°C in a circulating air oven in three different environments as follows:

1. In free air
2. Sealed in a glass tube in prepurified nitrogen.
3. Sealed in a glass tube with distilled water plus air.

In the second case, the tube and sample were pumped down to 0.1 micron of mercury and brought back to atmospheric pressure with prepurified nitrogen three times before being sealed off in this gas at approximately atmospheric pressure. The times required for the coating on the wire to develop typical "stress-cracks" of the kind shown in Fig. 1 are given in Table I together with the densities of the original and treated samples as determined by density gradient column per ASTM Designation D-1505.

Figure 1

The relatively rapid failure of the specimen in air makes it clear that this particular polymer is quite susceptible to oxidation, paralleling the result reported by Kafavian (Ref. 13) for a similar material. That oxidation alone, possibly involving only the surface layers, and not a change in crystallinity is responsible for failure in this case is clear from the fact that the specimen in nitrogen developed no cracks nor even any evident loss of flexibility after five times longer exposure. The relative contributions of oxidation and of increased crystallinity to the observed density increase can be estimated from Fig. 2, where the densities of the original, the water- and the nitrogen-aged samples establish an approximate curve for this polymer in a density vs. time plot of the type characteristic of polyethylenes held at a moderately elevated temperature. The displacement from this curve of the 96-hour point for the air-aged sample suggests that about 50% of its observed density increase at the time of failure can be ascribed with reasonable assurance to oxidation.

The very short life of the specimen in water establishes that extreme susceptibility to environmental cracking is an outstanding characteristic of this particular polymer, since water is not normally considered a particularly active cracking agent. Viewed by itself in the absence of the other information, the water failure could easily be misinterpreted as demonstrating high susceptibility to thermal stress-cracking, a conclusion which in light of the nitrogen sample could hardly be further from the actual facts. Clearly it is essential that, in attempts to characterize the cracking behavior of polyethylenes, the experiments chosen be designed in a way such that distinction between environmental stress-cracking, thermal embrittlement and oxidative rupture is sharp and unambiguous.

B. Initiation and Propagation Mechanisms-Hypotheses

Delineation of what environmental stress-cracking actually involves is far more difficult than merely distinguishing it from superficially similar phenomena. Only a limited amount has been published thus far on possible mechanisms for its initiation and propagation. In earlier papers (Ref 2), it was hypothesized that the initiation step might involve adsorption of a monolayer of polar molecules (which could be water) on the surfaces of a micro- or submicrofissure in the surface of the polymer, with the adsorptive energy contributing a spreading pressure which, when added to the other stresses present, produces a resultant which exceeds the cohesive forces of the polymer at the apex of the fissure. The subsequent propagation step could be

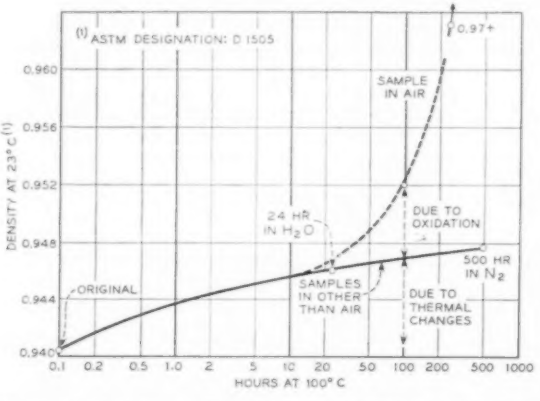


Figure 2. Changes in Density for an ASTM Type III Polyethylene With Time at 100°C in Several Media

TABLE I

Cracking Behavior of an ASTM Type III Polyethylene on Wire

Environment	Hours to Failure	Density*
None (original)	..	0.9405 ± 0.0004
Air at 100°C	96.	0.952 ± 0.001
Prepurified Nitrogen at 100°C	>500.**	0.9475 ± 0.0004
Water + Air at 100°C	24.	0.9460 ± 0.0004

* ASTM Designation: D-1505, After Exposure Indicated

** No Failure; remained flexible

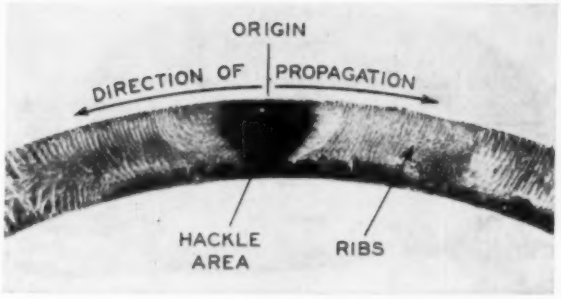


Figure 3.

visualized as aided by the extreme notch-sensitivity of these materials, with growth of the crack largely dependent on the availability of intercrystalline or interspherulitic boundaries traversed by relatively few polymer chains and held together chiefly by forces weaker than primary valence bonds (Ref. 4). The concentration of such interfaces in a given unit volume of polymer would be expected to increase with increases in the low molecular weight fraction of the polymer and with increasing size of the crystalline aggregates present. Kafavian (Ref. 13), too, has suggested that stress-cracking is dependent on the structure and characteristics of the material in the intercrystalline boundaries, and an hypothesis of the same general tenor is put forth in a paper by Heiss and Lanza (Ref. 14).

While the suggested mechanism has the merit of being consistent with the known facts, it has as yet no direct experimental confirmation, but advances in the electron microscopic techniques of solvent etching, replication and stereophotography offer bright promise for application to typical polyethylenes and fracture surfaces. It seems reasonable, nevertheless, that since environmental stress-cracking, thermal stress-cracking, and long-time brittle fatigue failure must all propagate through the same crystalline-amorphous complex, quite possibly even along identical paths, the phenomena must somehow be interrelated albeit they are initiated in different manners by different agencies.

C. Characteristics and Definition of Environmental Stress-cracking

As the name implies, the chief indentifying characteristic of environmental stress-cracking is the presence of an extraneous medium, in the absence of which the phenomenon does not occur. Effective media are usually but not always polar in nature and are not active solvents or swelling agents for polyethylene (Refs. 1, 2, 4, 35). Swelling agents can also produce cracks in stressed polyethylene, but these are the result of a general weakening of at least the surface layers of the polymer through plasticization and softening by the solvent (Refs. 2, 4, 35), and are not properly classified as environmental failures in the accepted sense, which always occur as ostensibly brittle fractures in unswollen surfaces.

A second unique feature of environmental cracking is its dependence on polyaxial stress. Ellis and Cummings (Ref. 15) found that it did not occur in susceptible cable sheath under uniaxial tension, and more recently Heiss and Lanza (Ref. 16) have reaffirmed this observation using flat specimens. Thermal stress-cracking, on the other hand, occurs in either uniaxial or polyaxial tension, as these last authors have shown. Since oxidative breakdown involves gross degradation of the polymer, it, too, would be expected to be insensitive to distinction between uniaxial and polyaxial stress.

The third distinguishing mark of environmental cracking is the apparently brittle character of the fracture produced (Ref. 2) and the presence of distinctive rib and hackle patterns (Ref. 5) reminiscent of those occurring in glass fractures. These patterns (cf. Fig. 3) often make it possible to determine the exact point of initiation and the direction of propagation of the failure (Ref. 17) under circumstances where this might otherwise be difficult or impossible. In ductile failures there is "necking down," fibering, or other evidence of plastic flow. Gross indications of such occurrences are not found in environmental cracking, except for an occasional small amount of cold-drawing at the terminus of a crack, the growth of which has destroyed the polyaxiality of the original stress.

Definite association with surface imperfections (Ref. 3, 35) also distinguishes environmental stress-cracking from purely thermal effects. A polyethylene which in the normal, "as molded" state fails completely in Igepal CO-630 (Ref. 18) at 50°C in less than 15 minutes may survive the same conditions indefinitely when the test specimens are heat-polished to seal over all surface flaws. In thermal stress-cracking, on the other hand, failure appears to be initiated within the mass of the plastic, well removed from surfaces and/or edges (Refs. 14, 20). Thus in environmental failures, both the initiation and the propagation of cracks appear to be associated intimately with the notch-sensitivity of these polymers, whereas in thermal cracking only the propagation step would seem to be so involved.

Having examined the identifying characteristics of environmental stress-cracking and the marks which distinguish it from superficially similar types of failure, it now appears feasible to define the phenomenon as follows:

> "Environmental stress-cracking is the failure in surface-initiated brittle fracture of a polyethylene specimen or part under polyaxial stress in contact with a medium in the absence of which fracture does not occur under the same conditions of stress. Combinations of external and/or internal stress may be involved, and the sensitizing medium may be gaseous, liquid, semisolid, or solid."

D. Influence of Major Variables

Despite the active interest in environmental stress-cracking in the plastics industry, there is as yet little in the literature on the effects of orderly changes in the major variables affecting this phenomenon. The practical difficulty of obtaining suitable series of samples

TABLE II

Melt Index as a Criterion of Stress-Crack Resistance

Sample	Melt Index	Cracking Time[2]
	G/10 Min	F_{20} (Hr)
1A	0.08	>1000
1B	0.22	>1000
1C	0.35	>1000
1D	0.60	>1000
1E	1.30	>1000
1F	7.80	0.25
1G	16	0.25
1H	64	0.25
1I	220	0.25
2A	0.08	>1000
2B	0.23	>1000
2C	0.60	5.0
2D	0.83	3.0
2E	1.40	2.0
2F	3.20	0.5
2G	14.8	<0.2

[1] ASTM Designation: D1238
[2] Bent-Strip Test in IGEPAL at 50°C

coupled with the known experimental problems in achieving reproducible crack test results may perhaps have proven too great an obstacle. Whatever the reason, while the literature does contain some statements as to the relative importance of certain variables, there is but little actual data to be found.

Average molecular weight is recognized as a dominant factor in establishing the environmental stress-crack resistance of polyethylenes (Refs. 4, 5, 11, 14, 19). Spohn and Frey (Ref. 11) have shown a generalized curve relating crack resistance to molecular weight in terms of melt index. Richards has noted (Ref. 4) the very sudden alteration, as molecular weight is increased, from susceptible to highly crack-resistant polymers. Unpublished data illustrative of this are shown in Table II, where melt index per ASTM Designation D 1238 serves as the criterion of molecular weight and crack-resistance is measured by the bent-strip test of DeCoste, Malm and Wallder. The times reported are those required for failure of 20% of the specimens (F_{20}).

For the first series shown in this tabulation, the abrupt change which Richards has pointed out occurs in the region between melt indices 1.3 and 7.8. However, in assessing data of this type, it must be remembered that since polyethylenes are not a unique single molecular species nor even a single homologous family of polymers, but rather embrace a polydimensional universe of different polymer types, a break point in environmental crack-resistance cannot be expected always at the same level of molecular weight. The second series of Table II, where the break occurs between melt indices 0.23 and 0.60, makes this clear. Furthermore, it is entirely possible to come upon melt index 1.3 polyethylenes with crack resistance superior to that of others of the same general type (i.e. same density range) whose melt indices are much lower, say 0.6. This is to say simply that melt index alone does not provide necessary and sufficient characterization of ethylene polymers. Samples 1E and 2C of Table II illustrate this point.

Average molecular weights can, of course, be calculated in a number of ways. Number-averages (M_N), weight-averages (M_W), and other more complicated kinds of averages have been used or sugested (Ref. 21). Weight-averages are strongly affected by the presence of a few very large molecules (Ref. 11), number averages by the proportion of small molecules in the aggregate. It is reasonable, therefore, that certain properties of polyethylene sensitive to one or the other of these extremes of molecular species should show a dependence on the corresponding type of molecular weight average. Insofar as melt index is a function of M_W, which Peticolas and Watkins (Ref. 22) have shown to be true over only limited ranges, samples 1D and 2C of Table II indicate that environmental crack resistance certainly is not heavily dependent on this type of average. A relationship to number-average, which could account for the observed sensitivity to the low molecular weight end of the distribution curve, might be more reasonable.

Molecular weight distribution has definitely been shown to be an important variable in environmental stress-cracking. Soon after the advent of cracking troubles with cable sheath in 1948 it was noted that, other things being equal, crack resistance is sensitive to the amount of solvent-extractable low polymer present, which serves as an indication of the breadth of molecular weight distribution involved. Data for a typical group of polymers from the same source, seen from

TABLE III

Effect of Variation in Chloroform Extractable Fraction

Sample	Melt Index[1] (G/10 Min)	Inherent[2] Viscosity	Density 25°C	$CHCl_3$-Extract (% By Wt.)	Cracking[3] Time F_{20} (Hr)	Biaxial Stress-Strain Props. Stress at Rupture (psi)	Strain at Rupture (%)
3A	1.0	1.042	0.9209	11.8	4	13,400	385
3B	1.0	1.040	0.9201	10.6	25	12,800	375
3C	1.0	1.066	0.9226	9.7	>1000	16,600	420
3D	1.0	1.063	0.9213	9.3	>1000	17,900	450
3E	1.0	1.052	0.9211	7.9	>1000	14,800	410

[1] ASTM Designation: D1238
[2] At 0.5 g/100 ml in Xylene at 85°C
[3] Bent-Strip test using IGEPAL at 50°C

their melt indices, viscosities, and densities to be closely similar, are given in Table III. The chloroform extracts were determined by reducing the material to a paper-like form by passing it repeatedly through the cold, tight rolls of a laboratory rubber mill, packaging it in extracted tea bag paper, and boiling for 30 minutes in distilled chloroform, after which the extract was evaporated to dryness and weighed.

For these materials, a sharp break in stress-crack resistance appears to occur at about 10% extractables and is accompanied by a less sharply defined change in biaxial tensile properties as determined using water pressure in the diaphragm test described by Hopkins et al (Ref. 2). Since molecular weight distribution is but one of several pertinent variables, not all polyethylenes can be expected to conform to this exact pattern, but curves published by Spohn and Frey (Ref. 11) show that in general a superior level of stress-crack resistance can be expected at a given melt index for polyethylenes of narrow as opposed to broad molecular weight distribution.

The importance of this variable in stress-cracking is confirmed by the improvement resulting when the lowest molecular weight material is eliminated from a poorly resistant polymer by crude fractionation. For example, removal of 9% of the low molecular weight fraction from a typically susceptible polyethylene by extraction with boiling benzene-isopropanol azetrope was found to raise the cracking time in Igepal CA-630 at 25°C from 6 hours to more than 2 months.

Crystallinity is also found to be very important in environmental stress-cracking. The stress-crack resistance of a given polyethylene can be altered substantially by differences in crystallinity introduced through variations in thermal history (Ref. 4). Some polymers which, when slow-cooled from the melt, crack in a few hours may survive the same test conditions indefinitely if tested immediately after shock-cooling (cf. Table IVa). The advantages of rapid cooling are transient (Refs. 5, 23), however, and cracking times shorten, as shown in Table IVb, for a crack-susceptible polymer, as the material reverts slowly with time to an equilibrium crystalline state intermediate to the shock-cooled and annealed conditions.

The metastability of stress-crack resistance in shock-cooled specimens demonstrated by the data of Table IVb is further substantiated by the curves of Fig. 4, where changes in density with time of exposure to temperature of 70°C in a circulating air oven are shown together with concomitant changes in crack resistance for two polyethylenes from different sources. The curves of Fig. 4 show how the densities of typical polyethylenes appear to approach asymptotic values with time of residence at a given temperature, starting from an "as molded" state representing rapid but not shock-cooling. It should be noted that these densities are determined after the sample has been brought back to room temperature, and not at 70°C. These apparently asymptotic density levels increase for higher residence temperatures, but are normally lower than the maximum density obtained by slow cooling from the melt.

It is significant that the stress-crack resistance curves for these two ASTM Type I polyethylenes show no parallel leveling off but continue to drop after the density curves have become essentially flat. This is taken to mean that crack resistance is sensitive to changes in *crystallite size* which continue after total crystalline content has reached apparent equilibrium at the temperature involved. Presumably the growth of crystallites makes for increased flexural stiffness which results in higher stress concentrations when the specimen is bent, and may also lead to the condition spoken of earlier where intercrystalline boundaries are developed across which relatively few polymer chains extend. Both these factors tend toward diminution of stress-crack resistance.

The significance of the sensitivity of polyethylene to differences in crystalline content and texture resulting from even minor variations in thermal history cannot be overstated. It contributes without doubt the most important single impediment to the development of satisfactory crack test procedures because it introduces

TABLE IVa

Effect of Cooling Rate on Stress-Cracking Bent Strip Test Igepal CO-630 at 50°C

	Cracking Time (F_{50} in Hours)	
	Sample A (Melt Index 1.7)	Sample B (Melt Index 0.25)
Cooled rapidly (cold H_2O quench)	2.1	>2000
Cooled slowly (15 min. in mold)	1.1	1070
Cooled 6-8°C/hour	0.5	8

TABLE IVb

Effects of Delay in Start of Test on Environmental Stress-Cracking in a Melt Index 2 Polyethylene

Conditioned at Room Temperature Before Test For:	Minutes to Crack in Igepal at 50°C: Shock-Cooled (Liquid N_2)	Annealed (Slow Cooled) From 150°C
1 day	210	<30
3 days	120	<30
7 days	120	<30
20 days	38	<30
36 days	<30	<30

[1] Bent-Strip test. 1st observation at 30 min.

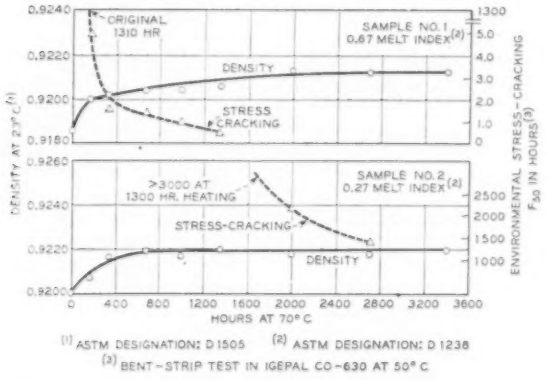

ORIGINAL 1310 HR
SAMPLE NO.1 0.67 MELT INDEX(2)
DENSITY
STRESS CRACKING
>3000 AT 1300 HR. HEATING
SAMPLE NO.2 0.27 MELT INDEX(2)
STRESS-CRACKING
DENSITY
DENSITY AT 23°C (1)
ENVIRONMENTAL STRESS-CRACKING F50 IN HOURS(3)
HOURS AT 70° C
(1) ASTM DESIGNATION: D 1505 (2) ASTM DESIGNATION: D 1238
(3) BENT-STRIP TEST IN IGEPAL CO-630 AT 50° C

Figure 4. Changes in Density and Environmental Stress-Cracking With Time at 70°C for Two Polyethylenes.

TABLE V

Change in Stress-Crack Resistance with Density

Sample	Melt Index (G/10 Min)	Density[2] at 23°C	Cracking Time[3] F_{50} (Hr)
5A	0.60	0.9218	>1000
5B	0.76	0.9320	7
5C	0.71	0.9415	>1000
5D	0.62	0.9472	130
5E	0.52	0.9492	200
5F	0.74	0.9502	12
5G	0.69	0.9573	72
5H	0.68	0.9613	12

[1] ASTM Designation: D1238
[2] ASTM Designation: D1505
[3] Bent-Strip test in IGEPAL CO-630 at 50°C

an uncontrolled variable of major consequence which can be removed only by standardized remelting of all test sheets and recooling them under rigorously controlled conditions. Universally reproducible means for accomplishing this are not yet available.

Gross variations in density arising from structural differences between polymers also have a large effect on stress-crack behavior. In general, stress-crack resistance can be expected to decrease as density increases, all other things being equal, but as can be seen in Table V other variables so becloud the issue that density differences do not furnish a reliable index of stress-crack resistance. Resulting differences in flexural stiffness, for one thing, so strongly affect cracking behavior that use of the bent-strip test is not recommended for comparing other than ASTM Type I polyethylenes (Ref. 24).

In addition to these structural variables, *the levels of stress and strain* imposed on the material have important bearing on its ability to withstand active environments (Ref. 35). Two fairly well-defined extremes can be recognized at the outset. Quite obviously, if there are no stresses involved, there can be no stress-cracking. A source of possible confusion here is the fact that the stresses need not be externally applied and so may not be immediately obvious. The less conspicuous "frozen-in" stresses and strains from molding or from handling at temperatures in the plastic range may be equally as effective as those externally applied (Ref. 35).

At the other extreme, when stresses and strains reach the levels at which cold-drawing takes place, physical displacement of the plastic dissipates the stress in systems not operating under constant load. If the experiment is so designed that the stress level is maintained, cold-drawing will proceed to its natural end-point, at which the strength properties of the original plastic will have been so altered that for practical purposes a different material is being tested. In round numbers, then, strains up to not more than about 50% are important in environmental stress-cracking, with the precise cutoff level depending on where the polyethylene in question begins to cold-draw.

A roughly analogous situation appears to exist for stresses. Carey (Ref. 25) has shown for the uniaxial case, and Richard, Diedrich, and Gaube (Ref. 26) have confirmed for polyaxial stresses, that the minimum stress at which brittle stress rupture will occur in the absence of a cracking agent varies with the molecular weight and crystallinity of the polyethylene involved, and that there appears to be a limiting stress for each polymer below which brittle failure does not occur. Presumably the introduction of an active cracking agent lowers this threshold by an amount which for most polyethylenes can only be surmised in the absence of data. Hittmair, Mark, and Ullman (Ref. 20) have shown that for one sample of 0.95 density coordination catalyst polymer, the limiting value of stress in Igepal CO-630 at 50°C appears to coincide approximately with the yield value of 2100 psi. This interesting observation merits further study.

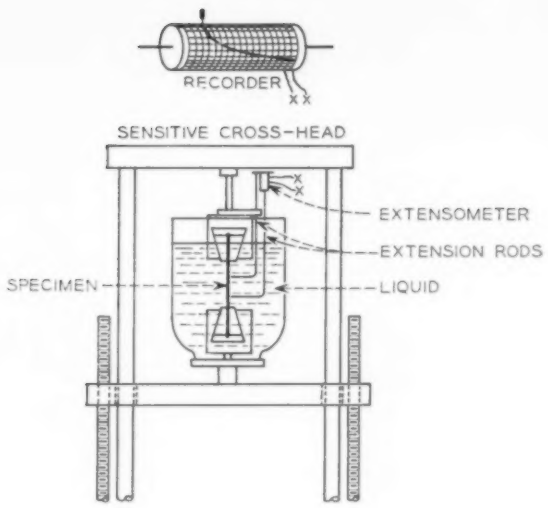
Thickness of sample cross section has a direct bearing on the level of stress concentration which can be built up in the sample by mechanical distortion (Ref. 19), and generally it will be found that for each polymer there is a thickness below which stress-cracking ceases to be a problem.

Molecular orientation can also influence the stress-crack behavior of polyethylene and must be considered especially when injection molded specimens or parts are involved. Uniaxial (fiber-type) orientation has long been known to enhance the strength of polymeric materials markedly in the direction of orientation, but at the expense of strength in the transverse direction. While there is little confirmatory information in the literature, it might be expected from the presumed nature of the stress-cracking phenomenon that such orientation would improve stress-crack resistance in the one direction and impair it in the other. Polyethylene doubly oriented by forces operating at approximately right angles to each other might similarly be expected to show stress-crack resistance generally superior to that of its unoriented state regardless of the directionality of the stress involved. Richard and his coworkers (Ref. 26) have confirmed that the limiting stress in water is higher for polyaxially oriented than for unoriented polyethylene pipe, but did not report on more active environments.

The chemical nature of the sensitizing medium has, of course, a large effect on the stress-cracking behavior of any susceptible polyethylene. In general, the "mobile polar liquids" cited by Richards (Ref. 1) are most dangerous since this class includes the alcohols, a majority of the very potent surfactants, and water. There is evidence to suggest that many materials which appear to be very active cracking agents may function primarily to accomplish wetting of the polyethylene surface by water. Heiss and Lanza have shown (Ref. 14), for example, that a sample of polyethylene containing an unusually high catalyst residue and characterized by an abnormally low wetting angle is very susceptible to stress-cracking in distilled water.

An important facet of the behavior of many active cracking agents is a low order of dependence on concentration. Surfactants, for example, can often be dangerous at quite low concentrations, presumably because adsorption tends to concentrate them from even dilute solution on the surfaces where their presence is most harmful (Ref. 27). Some materials, of which Igepal CO-630 is an example, actually become more vigorous cracking agents when diluted with water.

The catalog of materials which have been checked for stress-cracking activity is far too long to repeat here. DeCoste et al (Ref. 5), Bockhoff and Neumann (Ref. 27), and Pinsky (Ref. 28) have each given short compilations, and a more complete, previously unpublished list from our Laboratories is attached as Appendix A. From these data it is evident that while potentially dangerous materials can be found in a wide variety of sources, they are, in general, polar in nature and more or less mobile even if not always liquid in the accepted sense. An outstanding apparent exception



* R.H. CAREY ASTM BULLETIN NO.167, PP 56-60 (JULY 1950)

Fig. 5. Immersion Testing Apparatus*

is an instance of cracking of one polyethylene by another, a melt index 2.0 polymer by one of melt index 220 encountered by Wallder (Ref. 29).

Finally, *temperature* influences environmental stress-cracking. No definitive studies of this variable have been reported in the literature, but it is apparent from unpublished work of Wallder and his associates (Ref. 29) that over the range from about 25°-70°C, elevation of the temperature favors more rapid failure. Ranalli (Ref. 35) reports a similar conclusion. As the temperature is raised, creep rates increase also, and stress relaxation may become so rapid as to lead to anomalously long cracking times. At temperatures above 70°C this can be a very serious problem with Type I polyethylenes.

Test Procedures

A. Materials Test (as opposed to end-use tests)

1. Perforated Tensile Bar Immersion Test

The first published information on stress-cracking tests for polyethylene is that of Carey (Ref. 3) in 1950, who used injection molded tensile bars containing a stress-raiser in the form of a 1/16-inch diameter hole drilled through the flat face of the specimen at right angles to its long axis. By straining such specimens at the constant rate of 0.1" per minute in the apparatus shown in Fig. 5, Carey was able to make distinction between different molecular weight grades of polyethylene in the presence of certain solvent and non-solvent media. Data from his paper are shown in Fig. 6. While this test has the possible disadvantage of operating under neither constant stress nor constant strain, it has the great practical advantage of furnishing immediate results. It is, in the author's opinion, regrettable that more use has not been made of this procedure.

Quite recently Hittmair, Mark, and Ullman (Ref. 20) have begun to report results obtained with a constant-stress variation of the Carey test which eliminates one of the possible objections to the original procedure at the expense of immediacy of result. It also brings to the fore the question of whether such testing is better done under constant stress or constant strain. Possibly there may be applications for each.

2. Bent-strip Test

The best-strip test introduced by DeCoste, Malm, and Wallder (Ref. 5), sometimes called the Bell Laboratories Test, is the best-known of the environmental stress-crack procedures in use today. Although it suffers from certain limitations in its present form, it has nevertheless been proven a practical control test on many millions of pounds of polyethylene compound over a period of more than 10 years. Much of the failure for which it has been criticized arises, as we shall see, not from the test itself but from present inability to mold polyethylene reproducibly from laboratory to laboratory. The sensitivity of crack resistance to thermally induced variations in crystallity has brought to the fore this long-standing inability, which is basic to all crack test procedures.

As originally described, this test consists of punching ½" x 1½" specimens from 0.125-inch thick sheet with a die, cutting a stress-raising slit 0.020" deep by ¾" long parallel to the long axis of the specimen in the center of one of the ½" x 1½" faces with a special razor-blade jig, then bending these specimens double with the slit on the outside and inserting them into a 15 x 125 mm. test tube. The test tube is filled with cracking agent and placed in a 50°C thermostat. Suggested modifications of the original procedure include the use of special bending and insertion tools, brass channel specimen holders (cf. Fig. 7), replacement of Igepal CA Extra High Concentrate with Igepal CO-630 as the standard cracking agent, and attempts to use the 50% failure point (F_{50}) as the criterion of crack resistance in place of the more rudimentary go-no-go criterion used successfully for routine inspection and quality control purposes. This test has for several years been under study by a group in ASTM, which published details of an early version of the method in 1956 (Ref. 30) and has more recently released a status report and a modified version of the procedure (Ref. 24).

The largest available single body of interlaboratory test data using this test is that obtained in the first round robin conducted by Task Group 1 of Section J, Subcommittee XV, ASTM Committee D20. Twelve laboratories collaborated in obtaining these data using essentially the procedure published in 1956. The results, heretofore published only in the ASTM committee reports, are given in Tables VI and VII for all the tests involving the standard reagent and sample thickness. In the first of these two tables, where the data are reported in terms of F_{50}, conformance of the results from the several laboratories involved is seen to be quite good for twelve of the twenty samples involved, fair to poor for three others, and nonexistent for the remaining five samples. The over-all picture is, then, ragged and far from the level of reproducibility needed for a universal test procedure. It is from these data and those which followed in three other round robins that much of the present dissatisfaction with the method stems.

The same data are re-examined in Table VII on a pass-fail basis analogous to that used successfully for quality control purposes. The criterion here is 50% survival at 48 hours. On this basis, the one for which the procedure was originally suggested, agreement between the participating laboratories is seen to be 100% for 16 of the 20 samples involved, including even the 0.96 density material. Overall agreement for all 20 samples and 12 laboratories is 93.4%, a respectable showing for any test.

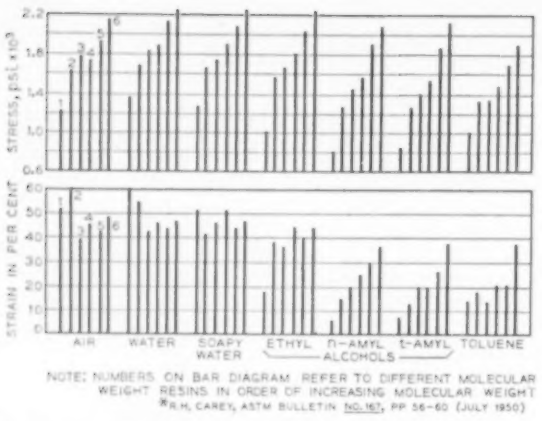


Figure 6. Breaking Stress and Strain of Specimens Containing A 1/16 in. Diameter Hole*

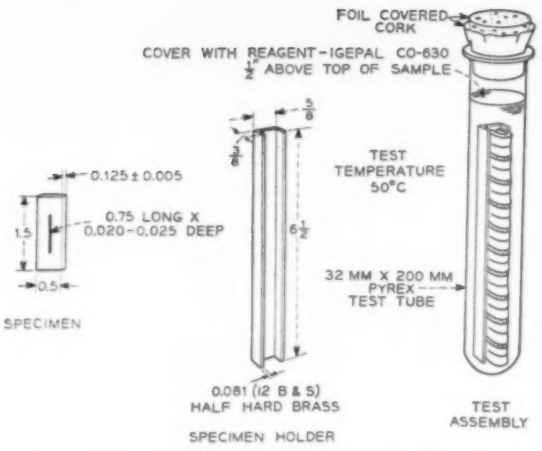


Figure 7. Specimen and Apparatus for Bent-Strip Test

An error, then, would seem to have been made in the attempt to use this procedure for precise F_{50} values at the present state of the art. This having proven impossible, there may be danger of compounding the error by a trend toward the other extreme and rejection of the method as totally worthless. This could be an equally serious error in view of the widespread demands for a cracking test since the data in Table VII plus over 10 years of use by the Bell System and its suppliers testify that the bent-strip test can, in spite of its limitations, serve a very useful purpose in development and quality control work when properly applied on a pass-fail basis. This approach is recommended for consideration as a stopgap until such time as the obstacles in the way of a more precise method can be overcome.

Although there are several reasons why the bent-strip test as presently written fails to give reproducible F_{50} values from laboratory to laboratory, unquestionably the most important of these is the demonstrated inability to control molding conditions, particularly the temperature cycle, used in preparing test specimens with the precision necessary for production of uniform crystalline content and texture between laboratories. In the second round robin conducted by the ASTM group, agreement was reasonably good among the participants testing specimens molded by one and distributed to the others, but very poor for the same polyethylenes molded by the laboratory doing the testing (cf. Table VIII). These data indicate that variations in molding procedure constitute a major variable in the stress-crack test.

Since without remelting, the density of molded polyethylene can change only in an upward direction, it might be argued from data such as that shown earlier in Fig. 4 that if molding conditions were so chosen that the density of the specimens produced always fell below their apparent equilibrium density at some moderately elevated temperature, such as 70°C, conditioning at this temperature for a suitable length of time should bring them to a reproducible standard state. In the hope of achieving such an effect, attempts have been made to override previous thermal history by boiling samples in water or by heating them in an oven. These efforts have proven only partially effective at best, possibly because the rate at which the material is cooled through the critical crystallization range during molding apparently not only establishes its crystalline content but also determines in large measure the size to which the crystallites and crystalline aggregates can eventually grow. The evidence available strongly suggests that the effects of prior thermal history can be eradicated only by remelting the test sheet and recooling it under precisely regulated, reproducible conditions. A practical procedure for so doing without distorting the sheet beyond tolerable limits has not yet been reported, but only after this problem has been solved can orderly attack begin on the lesser variables of the test procedure.

The more important of the minor variables affecting the reproducibility of the bent-strip test are thought to be:

(1) The curvature of the bent specimen, which is not rigorously controlled but is fixed primarily by the stiffness of the material, the more flexible polymers giving a smoother bend of larger radius with attendant lower stress concentration.

(2) Neither stress nor strain is maintained constant as the test progresses but both are allowed to decay (Ref. 26) at rates which probably vary from polymer to polymer. This reflects the origin of the test in simulation of conditions in a buckle thrown up during installation in the sheath of a telephone cable.

(3) The rate of stressing the specimens is not closely controlled. This is probably most serious with the higher density polyethylenes.

Each of these variables has received consideration at the hands of interested groups and individuals, but attempts to study them in an orderly fashion have been confused by the overriding effects of inadvertent variations in sample preparation. As a result, there is as yet no valid information available on how best to overcome them.

It cannot be stressed too strongly that the problem of mold-induced variations besets not only the bent-strip test, but also every other type of stress-crack test procedure and every other test for crystallinity-sensitive properties, density determination being one prominent example. It merits high priority on the list of most wanted polyethylene information.

3. Controlled Compression Test

Ranalli (Ref. 35) has reported work with a variation of the bent-strip test embodying a controlled rate of straining. He uses an unnicked 1-1/3" x ½" x ⅛" specimen coated with cracking agent and bent between the jaws of a specially designed compression machine. The upper jaw of this device is made to move down-

TABLE VI

Data from First Stress-Crack Round Robin—
Task Group 1, Section J, Subcommittee XV,
ASTM Committee D_2O

Cracking Time (F_{50}) in Hours [1]

Testing Laboratory	Sample→	A-1	A-2	A-3	B-1	C-1	C-2	C-3	C-4	D-1	D-2	E-1	E-2	E-3	E-4	K-1	K-2	K-3	K-4	K-5	R-1
	Melt Index[2]→	0.21	0.79	1.3	2.0	0.25	0.44	1.9	1.2	1.1	3.5	2.	2.	2.	7.	0.3	0.8	1.8	2.9	7.9	0.47
A		> 336.	5.3	0.4	> 336.								41.8					133.			10.3
B		> 336.	2.6	1.0	31.								2.0					39.3			16.3
C		> 193.	4.0	0.5	0.6							0.2	13.2	0.3				24.0			9.8
D				0.3		> 336.	> 336.	6.5	1.6				2.0					6.9			27.
E				0.7		> 336.	> 336.	85.	11.				1.4					> 336.			19.6
F				0.2		> 336.	> 336.	128.	2.4				0.6					17.			23.
G				0.7						> 336.	4.0	0.7	9.5	2.0	0.2			8.			
H				0.4						> 336.	3.0	0.7	2.6	2.6	0.2			46.			37.
I				0.2						> 336.	0.4	0.2	12.0	> 336.	0.3			> 336.			9.6
J				0.2						> 336.	8.5		0.9			> 336.	> 336.	3.2	1.0	0.3	9.8
K				0.4									0.3			> 336.	> 336.	6.3	1.3	0.2	11.7
L				0.6									1.1			> 336.	> 336.	3.5	1.3	0.2	10.3
	av.	> 200.	4.0	0.5	?	> 336.	> 336.	73.2	5.0	> 336.	4.0	0.5	7.3	?	0.2	> 336.	> 336.	?	1.2	0.2	16.8
	No. of Labs.	3	3	12	3	3	3	3	3	4	4	4	12	4	3	3	3	12	3	3	11

(1) Bent-strip test in Igepal CO-630 at 50°C. Test sheets molded from mill-massed material.
(2) ASTM Designation: D1238.
(3) ASTM Designation: D1248 Type III (all others Type I).

TABLE VII

Data from First Stress-Crack Round Robin—
Task Group 1, Section J. Subcommittee XV,
ASTM Committee D_2O

Pass-Fail Conformance to Criterion of
$F_{50} > 48$ Hours[1]

Testing Laboratory	Sample→	A-1	A-2	A-3	B-1	△-1	C-2	C-3	C-4	D-1	D-2	E-1	E-2	E-3	E-4	K-1	K-2	K-3	K-4	K-5	R-1[3]
	Melt Index[2]→	0.21	0.79	1.3	2.0	0.25	0.44	1.9	1.2	1.1	3.5	2.	2.	2.	7.	0.3	0.8	1.8	2.9	7.0	0.47
A		P	F	F	P								F					P			F
B		P	F	F	F								F					F			F
C		P	F	F	F							F	F	F				F			F
D				F		P	P	F	F				F					F			F
E				F		P	P	P	F				F					P			F
F				F		P	P	P	F				F					F			F
G				F						P	F	F	F	F	F			F			
H				F						P	F	F	F	F	F			F			F
I				F						P	F	F	F	P	F			P			F
J				F						P	F		F			P	P	F	F	F	F
K				F									F			P	P	F	F	F	F
L				F									F			P	P	F	F	F	F
	% Conformance	100.	100.	100.	67.	100.	100.	67.	100.	100.	100.	100.	100.	75.	100.	100.	100.	75.	100.	100.	100.
	No. of Labs.	3	3	12	3	3	3	3	3	4	4	4	12	4	3	3	3	12	3	3	11

OVER-ALL CONFORMANCE—20 SAMPLES, 12 LABORATORIES: 93.4%

(1) Bent-strip test in Igepal CO-630 at 50°C. Test sheets molded from mill-massed material.
(2) ASTM Designation: D1238.
(3) ASTM Designation: D1248 Type III. (All others Type I).

TABLE VIII

Effect of Molding Variations on Stress-Cracking
(Data from 2nd ASTM Round Robin)

Sample	Melt Index[1] G/10 Min	Cracking Time F_{50} in Hours[2]					
		Molded by Resin Supplier			Molded by Testing Lab		
		Min.	Max.	Av.	Min.	Max.	Av.
B-1	2.0	7.2	8.5	11.8	4.0	>336	?
C-2	0.44	>235	>336	>235	>336	>336	>336
K-3	1.8	28	79	63.8	3.2	>336	?

[1] ASTM Designation: D1238
[2] Bent-Strip test in IGEPAL CO-630 at 50°C

ward at a rate of 12 mm per minute against a lower jaw mounted on a compression spring coupled to an indicator showing the force exerted. He reports his results in terms of the separation remaining between the jaws and the load involved at the time of appearance of the first crack.

Application of this procedure is limited to materials which crack under the conditions imposed within the time required for the jaws of the testing machine to come together, about three minutes. For the polyethylenes on which Ranalli reports, this embraces melt indices of 0.6 and higher.

4. Diaphragm Test

Unpublished work by Wiebusch and Horn of these Laboratories led to the development of a test, based on the diaphragm test of Hopkins et al (Ref. 2), which overcomes one of the objections to the bent-strip test by operating at constant strain. A schematic presentation of the essential apparatus is shown in Fig. 8. It consists of a cup-like aluminum device holding a circular specimen cut from a polyethylene sheet clamped securely over a round opening in its top plate. This specimen is distended at its center by a steel ball impelled by a screw so calibrated that the strain introduced can be established approximately by the number of turns given the screw. Substitution of this mechanical straining device for the gas/liquid system in the original procedure greatly simplifies maintaining constant strain over long periods. Precise strains are determined by use of the silk screen technique described by Hopkins et al to apply a grid which is photographed immediately after straining the specimen, thus providing a record from which strain at the point of subsequent failure may be determined after the fact. The strained specimen is coated with cracking agent, placed in an oven at the test temperature and observed at regular intervals until failure.

Determination of the times required for failure at various levels of strain permits construction of a failure time vs. strain plot for the polyethylene being tested from which can be extrapolated a value for the limiting strain which the material can sustain in the presence of the test reagent at the temperature used. Typical curves for several polyethylenes in Igepal CA-630 at 50°C are shown in Fig. 9, from which it is apparent that polyethylenes differ in their limiting strains under the test conditions used. Some fail quite quickly under strains which others can tolerate indefinitely. These materials are all black cable sheath compounds of melt index as shown on Fig. 9. These data are reminiscent of those of Carey (Ref. 25) and Richard et al (Ref. 26) cited earlier.

Because it is time consuming, the test as described is not particularly attractive for routine inspection testing, but the character of the data it provides offers advantages over the bent-strip test for many development and analysis purposes. The test could, of course, be used on a pass-fail basis to ascertain routinely that material being used in a given application is capable of withstanding a predetermined strain for a given number of hours in the presence of a specified reagent at a specified temperature.

B. End-use Tests

1. General

In addition to the tests described in the preceding sections, three other environmental stress-crack tests whose objectives are to simulate conditions encountered in three specific applications of polyethylene have been reported in the literature. These differ substantially from each other in concept and operation. One, a modification of the bent-strip test using a different specimen, retains a limitation of the parent test in operating at neither constant stress nor constant strain. The second imposes a hoop stress at fixed strain on a molded ring. The third, utilizing an internally pressurized cylinder, operates under constant hoop stress to failure within the limits of the test assembly to maintain pressure.

Each of these tests is designed to provide information useful in a specific application. In addition to the variables noted as important in the preceding section, the test specimen in each of these cases embodies by the nature of its preparation other variables peculiar to the application in question, even though they may not always be recognized and under rigorous control. These tests are not intended and shouldn't be expected to serve as universal material tests. Both types of test are needed, the one for raw materials specification and quality control purposes to classify polyethylenes for inherent stress-crack resistance under rigorously controlled laboratory conditions, the other to satisfy the maker and the user of specific items fabricated from these materials that the added and possibly less rigorously controlled variables of the manufacturing process have not impaired the inherent crack resistance of the material unduly. On the basis, then, that each of these end-use tests serves a specific useful purpose, each will be considered briefly with attention to prominent individual characteristics.

2. American Agile Weld Test (Agile Test Method 17-W)

This test as described by Bockhoff and Neumann (Ref. 27) is designed to test the resistance of welded polyethylene corners and seams, such as might be used in large containers or liners, to the action of cracking agents. It is similar, except for the shape of the specimen and the resulting stresses, to the bent-strip test. Specimens are prepared by welding two ½" x 1½" strips of ⅛-inch thick polyethylene together along their ½-inch edges to form a right angle with beads of polymer filling both sides of the apex (cf. Fig. 10). The ends of the little "L"-shaped bracket so formed are spread apart by forcing the specimen into nearly flat configuration in a 20 x 200 mm. test tube containing the cracking agent.

The stresses imposed by this operation are different from those in a bent-strip, more closely resembling those exerted on the edge seam of a welded container or liner filled with liquid. Stress cracks may occur either in the polyethylene sheet stock or in the bead of the weld. Since the welding operation involves partial melting of the specimen, an added variable not present in the bent-strip test is introduced and must be controlled or its effects erased by adequate post-welding conditioning. The advantage of this test from the practical standpoint is, of course, its direct applicability to specimens cut from actual containers or liners.

3. Plax Bottle Test

The neck of any bottle is, of course, under stress when a stopper is forced into it or a cap screwed tightly into place. When the bottle is made of polyethylene and its contents may be a potential cracking agent, there is cause for concern. Quite early in the development of polyethylene bottles it became apparent that a practical environmental stress-crack test involving the essentials of this end-use was needed. Pinsky, Nielsen and Parliman have published (Ref. 28, 31, 32) a description of the simple but effective test developed in the laboratories of Plax Corporation for this purpose.

The specimen consists of the neck section of a 4 oz. Boston Round type polyethylene bottle. A tapered stainless steel plug is forced into the bottle mouth to an initial biaxial stress level of 800 psi and the assembly

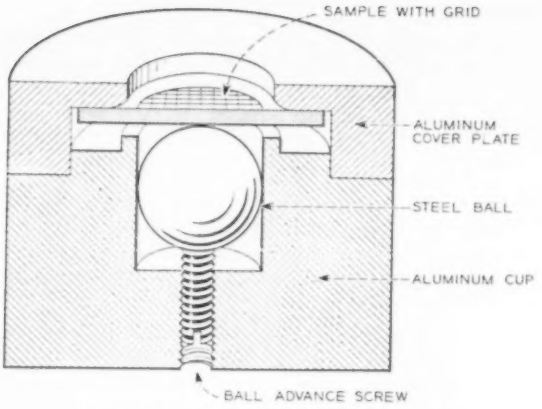
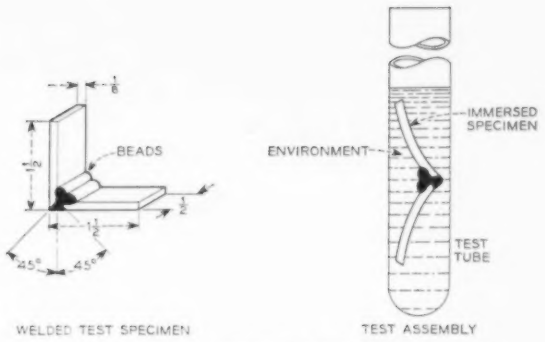


Figure 8. Schematic of Ball Test Apparatus.



*F.J. BOCKHOFF AND J.A. NEUMANN, SPE JL. 10, 17-19 (MAY 1954)

Figure 10. American Agile Weld Test*

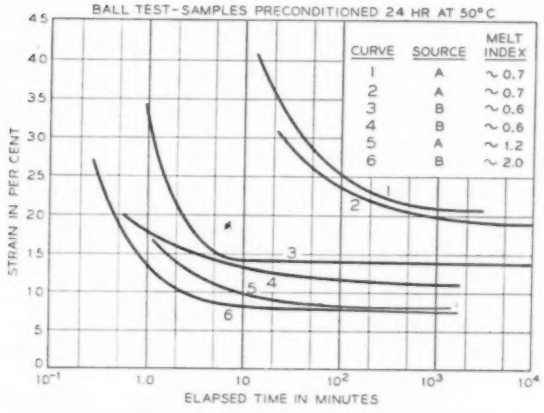


Figure 9. Limiting Strains in Igepal at 50°C for Six Samples of Polyethylene Cable Sheath Compound From Two Sources

then immersed in a pan of cracking agent (Igepal CO-630) at 25°C and observed for the appearance of cracks for up to seven days. By utilizing an actual bottle neck as the specimen, this procedure takes into account the effects of all the idiosyncrasies of the bottle-making process: molding strains, blowing orientations, and temperature variables none of which can be reproduced readily in another type of specimen.

No compensation is made in this procedure for the gradual relaxation of the specimen after the original stress is imposed. This stress therefore decays slowly beginning shortly after its imposition and the test, like those discussed earlier, does not operate at constant stress. Far from constituting a drawback in this case, however, this is in complete accord with normal use conditions, and the test proves excellent for evaluating the environmental stress-crack resistance of polyethylene bottles.

4. Pipe Tests

The stresses to which pipe is subjected in use differ from those imposed on cable sheath or on plastics bottles in that constant internal pressure is normally exerted on pipe. It is reasonable and proper, therefore, to test the environmental stress-crack resistance of pipe under constant stress in a procedure designed for the purpose. High precision in the reproduction of cracking times should not be expected, however, because in addition to the problems which beset sample preparation for the bent-strip test, pipe tests embody the multifarious variables peculiar to extrusion.

Hopkins (Ref. 2) employed a pressurized length of extruded tubing in some of his experiments, and pipe manufacturers and users have found similar procedures useful, if not always as reproducible as could be desired. Canadian Government Specification 41-GP-5A (Ref. 33) and Commercial Standard CS-197-57 (Ref. 34) are examples of working documents embodying such tests, but other references have appeared in the literature (Richard et al, [Ref. 26] for example). Details of the apparatus and cracking agent used, and the times, temperatures, and pressures involved are not always identical, and no attempt will be made to catalog them here. The basic principles of the test remain the same, however, and the Canadian Specification can serve as an example.

In this procedure a 10-inch length of pipe is clamped securely to fittings equipped with a pressure gauge and a check valve. The pipe is then inflated with air to 200% of the working pressure prescribed for its type and size. After being checked for leaks, the outer surface of the pipe is coated with cracking agent (Antarox A-203 in this case) and set aside at 70-80°F for 3 hours. No outright failures or incipient cracks visible to the unaided eye are permitted in six specimens.

Among the known variations of this procedure are the use of 250% of working pressure and continuation of the test with daily repressurization for as long as 500 hours on the part of manufacturers who wish to assure themselves of a superior quality level. Since this test, like the Plax Bottle Test, is made on the actual product, it has an unequalled advantage for its particular application. It should, however, be thought of as a go-no-go type of test rather than as one capable of yielding precisely reproducible failure times for the same reasons as apply in the case of the bent-strip test, chief among which is the extreme difficulty of universally reproducing test specimens exactly.

Summary

Superficially similar brittle fractures can occur in polyethylene from purely physical causes under three sets of circumstances identified as environmental stress-cracking, thermal stress-cracking, and static fatigue failure. These are initiated by different agencies acting in different manners, but seem to share a dependence on similar features of crystalline fine structure, which suggests they may be interrelated parts of one broader phenomenon.

Environmental stress-cracking, best known of the three, appears to owe its origin to the action of a sensitizing agent on minute flaws in the surface of polyaxially stressed polyethylene. It has been hypothesized that when the sum of the stresses developed within such flaws by adsorption of the agent plus the other stresses present exceeds the cohesive strength of the polymer, a crack results. Once initiated, the crack propagates through the polymer mass along the line of least resistance, which is suggested as possibly following intercrystallite boundaries bridged by relatively few polymer chains.

The major variables affecting the environmental stress-cracking of polyethylene are believed to be:

1. average molecular weight
2. molecular weight distribution
3. crystalline content
4. crystallite and/or spherulite size
5. the levels of stress and strain imposed
6. the presence or absence of orientation
7. the chemical nature and physical consistency of the sensitizing medium
8. the temperature involved.

The details of the thermal history of the polymer have a pronounced effect on its cracking behavior, presumably through modification of crystalline content and crystallite and/or spherulite size.

Environmental stress-crack test procedures now in use fall into two categories:

1. materials test not related to any specific application and useful for raw material specification and quality control purposes, and
2. end-use tests made on the vulnerable portions of specific items embodying all the variables of the fabrication process involved.

Both types of test serve useful purposes.

The available data show that the best known of these procedures, the bent-strip test, can be used effectively on a pass-fail basis in specification and control work. The fact that this method has not consistently yielded reproducible F_{50} times in interlaboratory tests is believed to be attributable primarily to present inability to prepare test sheets with a universally reproducible thermal history.

This same limitation applies to the other environmental cracking tests discussed, and affects tests for density and other crystallinity-sensitive properties as well.

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APPENDIX A

Cracking Observations on Stressed Melt Index 2 Grade Polyethylene in Contact with Various Environments

Bent-Strip Test Using Environments as Reagent

Test Observations

Environment	Source	Method of Application	25°C Reaction	25°C Days	50°C Reaction	50°C Days	Environment Rating	Comments
1.0 Components of Cable Sealing Compounds								
Indopol H-300	Stand. Oil of Indiana	Immersion			CR	7	Hazardous	Polybutene
Vistac 1	Oronite Chemical Co.	"			CR	12	"	"
" 4	" "	"			CR	19	"	"
Oronite 16	" "	"			CR	4	"	"
Flux A, asphalt	Stand. Oil of N. J.	Coating			OK	56	Safe	Hazardous at temps. above 50°C
" "	" "	"			CR	70*		
Flux 11, "	" "	"			CR	10*	Questionable	
Kendex 2430	Kendall Oil Co.	"			OK	192	Safe	Hazardous at temps. above 50°C.
" "	" "	"			CR	70*		
Pentoxide Asphalt P-100	Lion Oil Co.	Coating			CR	65*		Insufficient data at operating temperatures to apply a rating; probably safe below 50°C.
Pentoxide Asphalt G-120A	" " "	Coating			CR	40*		
Rosin Oil					CR	<1*	Hazardous	
Polyvinyl Isobutyl Ether	General Aniline & Film Corp.	Coating			CR	<1*	"	
DPR, High Viscosity	H. V. Hardman	Coating			CR	2	"	Depolymerized rubber
DPR, Low Viscosity	H. V. Hardman	Coating			CR	1	"	Depolymerized rubber
Cumar Resin AX	Barrett	Coating			CR	20	"	Component of LRM-294, List 2
2.0 Surface Active Agents								
2.1 Soaps								
Soap Solution, Summer Grade	Hollingshead	Immersion	CR	4	CR	1	Hazardous	Pressure testing soap
Coconut Potash, A	"	"	CR	125	CR	3	"	Component of pressure testing soaps
Triethanolamine Oleate	"	"	CR	1	CR	<1	"	Component of pressure testing soaps
Triethanolamine Stearate	"	"	CR	11	CR	<1	"	Component of pressure testing soaps
Dresinate 731	Hercules Pwd. Co.	"			CR	<1	"	Rosin Soap
" 7N70	" " "	Immersion			CR	<1	"	Rosin Soap
Castile Soap	" " "	"			CR	1	"	10% aqueous solution
Green Soap	Eimer & Amend	Coating			CR	2	"	Soft soap applied as a paste
" "	" "	Immersion			CR	1	"	10% aqueous solution
Ivory Soap	Procter & Gamble	Coating			CR	2	"	Rubbed onto the surface of the specimens
" "	" "	Immersion			CR	4	"	10% aqueous solution
Lead Oleate	" "	Coating			CR	5	"	
XX Special	Davis-Young	Coating	CR	<1	CR	2	"	Cable lubricant found to produce sheath cracking
Flaxsoap	Sherwin-Williams	Coating			CR	1	"	Lubricant for vinyl-jacketed wire
Olive oil base	Armour	Coating			CR	2	"	Lashing wire drawing compound; 2% and 50% solutions

* Test temperature 65°C

2.2 Synthetic Surface Active Agents

D. C. Antifoam	Dow-Corning	Coating			CR	1	Hazardous	Silicone Compound
Aquarex D	E. I. Dupont	Coating			CR	6	"	Sodium-Chloral sulphate
Carbona Soapless Lather		Immersion			CR	1	"	
Igepal CA, extra	General Dyestuff Corp.	"	CR	1	CR	<1	"	Alkyl aryl polyethylene glycol ether
Antarox 1835-186	General Aniline & Film Corp.	"			CR	17	"	Alkyl aryl polyethylene glycol ether
" A-200 (Igepal C.A. Ex)	" " "	Coating			CR	<1	"	" " " " "
" 1835-171	" " "	Immersion			CR	<1	"	" " " " "
" A-180	" " "	"			CR	<1	"	" " " " "
" 1835-175	" " "	"			CR	5	"	" " " " "
" 1835-173	" " "	"			CR	<1	"	" " " " "
Maypon, Special No. 2	Maywood Chem. Co.	Coating			CR	<1	"	
" OW	" "	"			CR	<1	"	
" 4C Cream	" "	"			CR	<1	"	
" 4C	" "	Immersion			CR	<1	"	
" super K	" "	"			CR	<1	"	
" K	" "	"			CR	<1	"	
Span 20	Atlas Powder Co.	"			CR	<1	"	Non-ionic compounds based on sorbitan
" 85	" "	"			CR	<1	"	" " "
Tween 20	" "	"			CR	<1	"	" " "
" 21	" "	"			CR	<1	"	" " "
G-1295	" "	Coating			CR	3	"	" " "
G-2130	" "	Immersion			CR	<1	"	" " "
Nyon 218	Sharples Chem. Corp.	"	CR	<1	CR	2	"	
Pensolve	Penetone Co.	"			CR	3	"	
Armac T	Armour & Co.	Coating			CR	<1	"	
Aerosol OT	Am. Cyanamid & Chem. Co.	Immersion			CR	3	"	10% aq. sol.; dioctyl ester of sodium sulfo succinate

2.3 Natural Surface Active Agents

Creamy Head	Snow White Co.	Immersion			OK	174	Safe	
Egg White		Immersion	OK	74	OK	74	"	
" "		Coated	OK	74	OK	74	"	
Hydrolyzed Soya Protein CF	General Bearing Cl. Co.	Immersion			OK	109	Safe	
" " " NF-2	" " "	"			CR	110	Questionable	Concentrated, considered as base for pressure test fluid.
" " " NF-3	" " "	"			OK	111	Safe	
" " " NF-6	" " "	"			OK	111	"	
" " "(NF-6+ Anti Freeze)	" " "	"			OK	144	"	
Hydrolyzed Soya Protein	Pyrene Mfg. Company	"			OK	288	"	
" " " " "	" " "	"			OK	288	"	5% aq. sol.
" " " " "	" " "	"			OK	288	"	1% aq. sol.

APPENDIX A (Continued)

Cracking Observations on Stressed Melt Index 2 Grade Polyethylene in Contact with Various Environments

Bent-Strip Testing Using Environments as Reagent

Test Observations

Environment	Source	Method of Application	25°C Reaction	25°C Days	50°C Reaction	50°C Days	Environment Rating	Comments
2.3 Natural Surface Active Agents (Cont'd)								
Hydrolyzed Soya Protein E-274	Pyrene Mfg. Company	Immersion			OK	135	"	Concentrated and 5% aq. sol.; contained fungicide, 5% aq. sol.; contained fungicide
E-275	" " " "	Immersion			OK	135	"	
Saponin, A107	Eimer & Amend	Immersion			OK	53	"	
" Toxic	Eimer & Amend	Immersion			CR	14	Hazardous	Acidic saponins have been found safe while basic saponins have caused cracking. All saponins were tested as 5% aqueous sol.
"	S. B. Penick	Immersion			OK	224	Safe	
Saponin	Baker	Immersion			CR	14	Hazardous	
"	Lemke	Immersion			CR	7	"	
Gum Arabic		Immersion			OK	217	Safe	5% aqueous solution
Dimethyl Hydantoin Formaldehyde Resin	E. I. Dupont	Immersion			OK	108	Safe	50% aqueous solution
2.4 Cellulose Base Testing Fluids								
Carboxy Methyl Cellulose	Hercules Powder Co.	Coating			CR	10	Hazardous	
Hydroxyethyl Cellulose	Carbide & Carbon	Immersion	OK	125			Safe	
Methocel Fluid	"	"	OK	125	OK	33	"	1.8% Sol. of Dow 15 cps. Methocel in water.
3.0 Duct Sealing Compounds and Gasketing Materials								
Barnard Duct Seal	B. S. Barnard & Co.	Coating			OK	205	Questionable	Probably contains hazardous oils
Cauzseal	X-Pando Corp.	"			CR	205	Questionable	
J. M. Ductseal	Johns-Mansville	"			CR	52	"	
J. M. Duxseal	" "	"			CR	106	"	
J. M. Uniseal	" "	"			OK	205	"	Probably contains hazardous oils.
Duct Seal	H. B. Morse & Co.	"			CR	20	"	
Tempseal	National Eng. Products Inc.	"			CR	22	"	
Neoprene M-194	B. T. L.	Laminate			OK	120	Safe	Cured; contains 20 pts. Golden Bear L. P. Oil.
Neoprene M-194A	B. T. L.	Laminate			OK	120	Safe	Cured; Contains 20 pts. Golden Bear L. P. Oil +3 pts. Helizone.
Neoprene M-194A	B. T. L.	Laminate			OK	120	Safe	Cured, contains 20 pts. Golden Bear L. P. Oil +3 pts. Herron Wax
Neoprene 46-189	B. T. L.	Laminate			OK	120	Safe	Cured; contains Circo Oil, L.
4.0 Miscellaneous Cable Environments								
DC-4 Silicone Comp.	Dow Corning	Coating	CR	<1	CR	<1	Hazardous	Used for waterproofing high tension systems. See Sec. 7.
Yellow Marking Crayon	Binney & Smith	Coating			OK	191	Questionable	Hot cable marked with crayon reported to crack.
6.0 Submarine Cable Environments								
6.1 Slushing and Weatherproofing Compounds								
Socony Asphalt, AP-4	Socony Vacuum Oil Co.	Coating			OK	116	Safe	
Solar Asphalt, KM-378	Solar Compds. Corp.	"			CR	115	Questionable	
Texaco Asphalt, #45	Texaco	"			OK	55	Safe	
Simplex #32 Compd.					OK	177	Safe	
" #56	Simplex Wire	"			OK	178	Safe	
" #36	&	"			OK	178	Safe	
" #51	Cable Co.	"			OK	177	Safe	
" Limestone		"			OK	177	Safe	
6.2 Jute Treating Compounds								
Lime Bath	Schlichter	Immersion			CR	13	Hazardous	
Oil Emulsion	"	"			CR	13	Hazardous	
Mineral Oil	"	"			CR	22	Hazardous	
Cutch	"	"			OK	86	Safe	
Emulsifier	"	"			CR	<1	Hazardous	
7.0 Oils and Plasticizers								
7.1 Mineral Oils (Note: Oils are arranged in the approximate order of increasing viscosity.)								
Kerosene	Stock Room	Immersion			OK	125	Questionable	
Bayol D	Stand. Oil N. J.	"			CR	1	Hazardous	
Cold Stripping Oil	W. S. Wilson Corp.	"			CR	3	Hazardous	
Golden Bear, Lt. Process Oil	Golden Bear Oil Co.	"			CR	2	Hazardous	Neoprene plasticizing oil.
Circo, Lt. Process Oil	Sun Oil Co.	"			CR	5	Hazardous	Neoprene plasticizing oil.
Tycol Aparil #91		"			CR	14	Hazardous	Neoprene plasticizing oil.
Esstic #45	Std. Oil of N. J.	"			CR	2	Hazardous	
Nujol		"			CR	1	Hazardous	
Motor Oil, S.A.E. 30		"			CR	1	Hazardous	
Coastal Pale	Adams-Cook	"			CR	4	Hazardous	
Pennsylvania Neutral	" "	"			CR	4	Hazardous	
Paraffinic White Oil	" "	"			CR	4	Hazardous	
Pennsylvania Bright Stock	" "	"			CR	19	Hazardous	
Coastal Bright Stock	" "	"			CR	39	Hazardous	
Sun XX Cable Oil	Sun Oil Co.	"			CR	9	Harazdous	Impregnating oil for paper insulated power cables.
Cyclesso T-140	Std. Oil of N.J.	"			OK	201	Questionable	Heavy gear oil.
Esso 600W	" "	"			OK	162	Questionable	Heavy gear oil.
Kendex #0834	Kendal Refining Co.	Coating				126	Hazardous	
" "	Kendal Refining Co.	Coating			CR	126	Hazardous	

APPENDIX A (Continued)

Cracking Observations on Stressed Melt Index 2 Grade Polyethylene in Contact with Various Environments

Bent-Strip Testing Using Environments as Reagent

Test Observations

Environment	Source	Method of Application	25°C Reaction	25°C Days	50°C Reaction	50°C Days	Environment Rating	Comments
7.2 Vegetable and Animal Oils								
Castor Oil		Immersion			CR	<1	Hazardous	
Lard Oil		"			CR	4	Hazardous	
Linseed Oil		Immersion			CR	1	Hazardous	
Pine Oil		"			CR	1	Hazardous	
Rosin Oil		"			CR	5	Hazardous	
Soya Oil		"			CR	1	Hazardous	
Oleic Acid		"	OK	125	CR	2	Hazardous	
Turpentine		"	CR	73			Hazardous	
7.3 Synthetic Oils and Plasticizers								
Abalyn	Hercules Powder Co.	Immersion			CR	4	Hazardous	Methyl ester of rosin
Dibutyl Phthalate		"	CR	20	CR	5	Hazardous	
Dioctyl Phthalate		"			CR	8	Hazardous	
Dioctyl Sebacate		"	OK	125	CR	5	Hazardous	
Paraplex G-25	Rohm & Haas	Coating			CR	4	Hazardous	
Tricresyl Phosphate		Immersion	CR	3	CR	<1	Hazardous	
Hydrogenated Ester Gum	Farboil	"			CR	7	Hazardous	
Silicone Fluid 200	Dow Corning	"			CR	<1	Hazardous	See Sec. 4.0
Ucon Lubricant 50-HB-5,100	Carbide & Carbon	"			CR	<1	Hazardous	Polyalkylene glycols and derivatives.
Ucon Lubricant 75-HB-9,000	Carbide & Carbon	"			OK	120	Questionable	Polyalkylene glycols and derivatives.
Ucon Lubricant 50-HB-660	Carbide & Carbon	"			CR	<1	Hazardous	Polyalkylene glycols and derivatives.
Ucon Lubricant 260	" "	"			CR	<1	Hazardous	Polyalkylene glycols and derivatives.
Carbowax 4000	" "	"			CR	120	Hazardous	60% solution polyalkylene glycol.
8.9 Organic Chemical Compounds								
Acetic Acid, glacial		Immersion	CR	4			Hazardous	
Acetone		"	CR	5			Hazardous	
Amyl Alcohol		"	CR	3			Hazardous	
Benzene		"	OK	125			Questionable	Physical properties degraded by high solvent absorption.
Benzyl Alcohol		"	CR	4			Hazardous	
Butyl Acetate		"	OK	125			Questionable	Possibly hazardous at 50°C.
Butyl Alcohol		"	CR	1			Hazardous	
Butyric Acid		"	CR	32			Hazardous	
Carbon Tetrachloride		"	CR	4			Hazardous	
Cresol		"			CR	1	Hazardous	
Cyclo-hexanone		"	OK	66			Questionable	Possibly hazardous at 50°C.
n-Caproic Acid		"	CR	397			Questionable	
n-Dolecane		"			CR	1	Hazardous	
Dipropylene Glycol		"	CR	5	CR	3	Hazardous	
Diethylene Glycol		"			OK	410	Safe	
Ethyl Alcohol		"	CR	3			Hazardous	
Ethylene Dichloride		"	OK	125			Questionable	Physical properties degraded by high solvent absorption.
2-Ethylhexoic Acid		Immersion			CR	5	Hazardous	
Ethyl Ether		"	OK	125			Questionable	
Ethylene Glycol		"			OK	516	Safe	
Furfural		"			CR	38	Hazardous	
Glycerol		"			OK	516	Safe	
Hexane		"	CR	14			Hazardous	
Methyl Alcohol		"	CR	17			Hazardous	
Naphtenic Acid		"			CR	13	Hazardous	
Nitro-Benzene		"	CR	17			Hazardous	
n-Octadecane		"			CR	6	Hazardous	
Pyridene		"	CR	7			Hazardous	
Toluene		"	CR	7			Hazardous	
Tetralin		"	CR	125			Hazardous	
9.0 Aqueous Solutions of Chemical Compounds								
Acetic Acid		Immersion			OK	175	Questionable	10% aq. solution; conc. acetic acid cause cracking. See Sec. 8.0
Ammonium Chloride		"			CR	24	Hazardous	50% aqueous solution
Ammonium Hydroxide		"			OK	77	Questionable	Hydrolyzes fats and oils to form soaps.
Borax		"			CR	130	Questionable	Saturate sol. (Less than 10%)
Calcium Chloride		"			OK	77	Safe	10% aqueous solution
Calcium Oxide		"			OK	175	Safe	" " "
Calcium Carbonate		"			OK	291	Safe	" " "
Citric Acid		"			OK	77	Safe	" " "
Dextrose		"			OK	77	Safe	" " "
Formaldehyde		"			OK	77	Safe	" " "
Potassium Dichromate		"			OK	77	Safe	" " "
Potassium Hydroxide		"			CR	6	Hazardous	" " "
Sodium Carbonate		"			CR	10	Hazardous	" " "
Sodium Chloride		"			OK	382	Safe	" " "
Sodium Sulphite		"			OK	217	Safe	5% " "
Sodium Sulphate		"			OK	217	Safe	" " "
Sodium Silicate		"			CR	7	Hazardous	Saturated Solution
Tannic Acid		"			OK	261	Safe	5% aqueous solution.
Urea		"			OK	77	Safe	10% and 50% aqueous solution.
					OK	77	Safe	10% aqueous solution.
Tannic Acid		"			OK	108	Safe	50% aqueous solution.
Zinc Chloride		"			OK	364	Safe	
Water, distilled		"			OK	154	Safe	
Water, tap		"			OK	46	Safe	
Water, H_2S saturated		"						

APPENDIX A (Continued)

Cracking Observations on Stressed Melt Index 2 Grade Polyethylene in Contact with Various Environments

Bent-Strip Testing Using Environments as Reagent

Test Observations

Environment	Source	Method of Application	25°C Reaction	25°C Days	50°C Reaction	50°C Days	Rating Environment	Comments
10.0 Gases								
Air		Atmospheric Press			OK	516	Safe	
Air		3 psi			OK	406	Safe	
Sulphur Hexafluoride		" "			OK	406	Safe	
Hydrogen Sulphide		" "			OK	406	Safe	
Propane		" "			OK	406	Questionable	
Carbon Monoxide		" "			OK	407	Questionable	(Cell showed no positive pressure at end of run)
Methane		" "			OK	406	Questionable	
Illuminating Gas		" "			OK	403	Questionable	
11.0 Tapes and Tape Compounds								
11.1 Rubber and Friction Tape								
CR Compound	U. S. Rubber	Coating			OK	193	Safe	
DR	" "	Coating			OK	193	Safe	
Neoprene Adh. Compd.	" "	Coating			OK	193	Safe	
#5588 Friction Tape Comp.	" "	Coating			OK	193	Safe	
11.2 Aluminum Tapes								
Vistanex Tapes	International Plastics	As tape			OK	191	Safe	
Vistanex Tapes	Minnesota Mining Co.	" "			OK	191	Safe	
Vistanex Tapes	Ind. Tape Corp.	" "			OK	191	Safe	
Nat. Rubber Tapes	Ind. Tape Corp.	" "			OK	191	Safe	
ST-951 Compd.	Ind. Tape Corp.	Coating			OK	185	Safe	
11.3 Miscellaneous Tapes								
Paper Cable Paster Tape		As Tape			OK	94	Safe	
Scotch Electrical #3	Minnesota Mining Co.	" "			OK	124	Questionable	Paper back, Dec. 1949
Scotch Electrical #27	Minnesota Mining Co.	" "			OK	124	Safe	Glass clothback, Jan., 1950
Plastic Tape	Bishop Gutta Percha Co.	" "			OK	69	Safe	Polyethylene Polyisobutylene Compound
12.0 Fungicides								
Nuodex X209	Nuodex Prod. Co.	Coating			CR	15	Hazardous	
Nuodex 100 WD	Nuodex Prod. Co.	Immersion			CR	<1	Hazardous	An ammonium cyclopentane carboxolate salt.
Nuodex 100 SS	Nuodex Prod. Co.	Coating			CR	<1	Hazardous	
Nuodex 100 Conc.	Nuodex Prod. Co.	"			CR	<1	Hazardous	
8 Hydroxquinoline	Eastman	Immersion			OK	123	Safe	10% sol. in dilute aqueous acetic acid.
8 Hydroxquinoline Sulphate	Eastman	"			OK	127	Safe	10% aqueous solution
Milmer 1	Monsanto Chem. Co.	Dry Powder			OK	129	Safe	Copper-8-Hydroxquinoline
Sodium Pentachlorophenate		Immersion			CR	18	Hazardous	10% aqueous solution
#344-B Fungicide	Gen. Bearing Cleaning Corp.	Immersion			OK	223	Safe	Strong phenolic odor, questionable from a dermatological basis.
Sodium Propionate	Gen. Bearing Cleaning Corp.	"			CR	106	Hazardous	5 and 10% aq. solutions.
13.0 Insecticides								
Dr. Lobel's DDT Sol.		Coating			OK	132	Questionable	5% of DDT in light petroleum oil plus pyrethrum. Immersion in this mixture would undoubtedly cause cracking.
DDT		Powder			OK	97	Safe	Dichlor-diphenyl-trichlorethane
14.0 Weed Killers								
2-4-D Concentrate	Sears Roebuck	Spray Coating			CR	3	Hazardous	2-4 dichlor phenoxy acetic acid
2-4-D plus 2-4-T		Immersion			CR	<1	Hazardous	Dispersed in butyl cellosolve and diesel oil
Esteron 44 (2-4-D) plus Esteron 245 (2-4-5-T)		Immersion			CR	2	Hazardous	2 qts. Esteron 44 and 2 qts. Esteron 245 per 100 gal. water.
Esteron 44 (2-4-D) plus Esteron 245 (2-4-5-T)		Immersion			CR	1	Hazardous	2-½ qts. Esteron 44 and 2-½ qts. Esteron 245 per 30 gals. kerosene
Ammonium Sulfamate		Immersion			OK	192	Safe	1 lb. per gal. of water
15.0 Orchard Sprays								
Sulphur		Powder			OK	115	Safe	
Arsenate of lead		Aq. Paste Coating			OK	272	Safe	
Benzene Hexachloride		Powder			OK	228	Safe	
Benzene Hexachloride Sol.		Coating			CR	<1	Hazardous	Dissolved in a kerosene-tallow vehicle.
Benzene Hexachloride Sol.		Immersion			CR	<1	Hazardous	Dissolved in a kerosene-tallow vehicle.
Black Leaf "40"		Spray			OK	253	Safe	Nicotine sulphate; often used with 2 surface active agent which would form a hazardous mixture.
Copper Hydro		Aq. Paste Coating			OK	272	Safe	
Lime-sulphur		Immersion			OK	41	Safe	5% aqueous mixture.
Lime-sulphur		Aq. Paste Coating			OK	273	Safe	

H. W. Coover, Jr. received his B.S. Degree from Hobart College and M.S. and Ph. D. from Cornell University. He joined Eastman Kodak research staff in 1944. In 1950 he transferred to the Research Laboratories of Tennessee Eastman Co., where he is now research associate.

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Chemistry and Performance of Cyanoacrylate Adhesives

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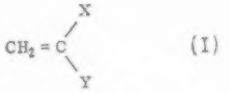
Research Laboratories
Tennessee Eastman Company
Division of Eastman Kodak Company

THE ADHESIVE ACTION of alkyl 2-cyanoacrylates was discovered during an investigation of a series of polymers derived from 1, 1-disubstituted ethylenes. A drop of highly purified ethyl 2-cyanoacrylate was placed between the prisms of an Abbé refractometer in order to obtain its refractive index for comparison with that of a previously prepared sample. When an attempt was made to open the refractometer, the prisms could not be pulled apart.

As a result of this discovery, the properties of the 1, 1-disubstituted ethylenes (I) as adhesives were studied.



(I)

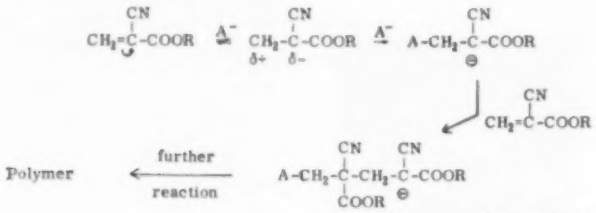
It was found that certain compounds of this type, in which *X* and *Y* are strongly electronegative groups, exhibit unusual properties which make them the basis for a radically new type of adhesive (Refs. 1-7). Of the various vinyl-type monomers studied, the alkyl 2-cyanoacrylates appeared most promising. Conventional adhesives function by application of heat and pressure, addition of a catalyst, or evaporation of a solvent (Ref. 8). The alkyl 2-cyanoacrylates are converted from the liquid to the solid state by polymerization when pressed into a thin film between two adherends. This polymerization occurs at room temperature and does not require the use of a solvent or an added catalyst. Unusually strong bonds are produced rapidly with a wide variety of adherend combinations.

It is the purpose of this paper to discuss the mechanism of the adhesive action of the alkyl 2-cyanoacrylates

and to describe their performance under a variety of test conditions.

THEORY OF ADHESIVE ACTION

Negatively disubstituted ethylenes of the type represented by (I) polymerize by a base-catalyzed ionic mechanism; for example, the alkyl 2-cyanoacrylates readily undergo a highly exothermic polymerization which may be initiated at low temperatures by even very weak bases such as water and alcohols. This polymerization reaction is represented by the following equations in which the basic catalyst is represented by A^-, an electron donor:



(Formula 1)

The bonding action observed when a 2-cyanoacrylate is placed between two adherends is the result of this anionic polymerization. This polymerization is apparently catalyzed by minute amounts of water or other weak bases present on the adherend surfaces. Their effect on the bonding action is maximized by spreading the adhesive monomer into a very thin film. Acidic substances exert an inhibitory effect on the polymerization and thus can be used as stabilizers.

All such negatively disubstituted ethylenes do not possess the phenomenal activity associated with the alkyl 2-cyanoacrylates. Monomers possessing electronegative groups which function primarily through a strong inductive (–I) effect do not possess the sensitivity of the 2-cyanoacrylates toward weak bases; for example, 2-(trifluoromethyl)acrylonitrile and methyl 2-(trifluoromethyl)acrylate are not polymerized by weak bases such as water or alcohols, although the trifluoromethyl group is strongly electronegative.

The sensitivity of the alkyl 2-cyanoacrylates to weak bases, which effectively catalyze the polymerization of these monomers, is probably due to the strong electromeric (–*E*) effects of both the nitrile group and the alkoxycarbonyl group. Under the influence of the catalyst, the strong –*E* effects which are brought into play render these groups strongly electronegative. When the –*E* effects of groups of this type are strong and are operating, the electronegativity generally overshadows that of any group operating only through a strong –I effect. Thus, the combined –*E* effect of the nitrile group and the alkoxycarbonyl group, stimulated by even very weak bases, is apparently sufficient to cause an unusually strong polarization of the double bond in the alkyl 2-cyanoacrylates:

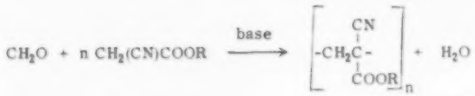
(Formula 2)

It may be concluded that for monomers of the type shown (I) to be useful in the new type of adhesives represented by the alkyl 2-cyanoacrylates, strong –*E* effects must be capable of operating in both *X* and *Y*.

DISCUSSION

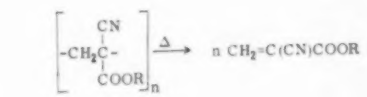
Preparation and Stabilization of Monomers

Alkyl 2-cyanoacrylates are produced by condensing formaldehyde with an alkyl cyanoacetate in the presence of a basic catalyst to yield first a poly(alkyl cyanoacrylate) (Refs. 9-13):



(Formula 3)

Depolymerization of this material yields the alkyl 2-cyanoacrylate:



(Formula 4)

Redistillation of the crude monomer is necessary to provide monomer which is active enough for use in adhesives. For example, methyl 2-cyanoacrylate, when pure, polymerizes spontaneously on warming to room temperature. Certain acidic substances inhibit this polymerization (Ref. 14) and yet permit the monomer to polymerize when spread in a thin film between two potential adherends.

Monomeric alkyl 2-cyanoacrylates are quite fluid. Addition of properly purified thickening agents to the monomers produces materials ranging from thin sirups to thick gels (Ref. 2). These viscous formulations are more suitable for general adhesive use than the fluid monomers.

Finally, the addition of plasticizers to the adhesive formulation has been found to overcome embrittlement of the bond during aging (Ref. 7). This improvement is accomplished without reducing the tensile strength of the bond.

Properties of Alkyl 2-Cyanoacrylates as Adhesives

Unlike most chemical solidifying reactions, the polymerization of alkyl 2-cyanoacrylates occurs without appreciable change in volume. This property probably accounts for the exceptionally strong bonds formed with a variety of adherend combinations and makes possible the use of certain viscous formulations as "gap-filling" adhesives. A consideration of the types of materials bonded with alkyl 2-cyanoacrylate adhesives indicates their ability to perform well in both specific adhesion (caused by molecular attraction with smooth, dense surfaces) and mechanical adhesion (caused by mechanical grip action or interlocking of the set adhesive in the surface irregularities, cavities, or pores of a rough surface of the solid adherend).

Although a number of 2-cyanoacrylic esters were prepared, data obtained using the adhesive formulation based on methyl 2-cyanoacrylate are presented to il-

TABLE I

Effect of Adherend Combination on Action of Methyl 2-Cyanoacrylate Adhesive

Bond Type	Bonding Action[a]	Bond Strength[b]
Glass-glass	Rapid	Strong
Aluminum-aluminum	Rapid	Intermediate
Steel-steel	Intermediate	Strong
Glass-rubber	Rapid	Strong
Porcelain-porcelain	Rapid	Strong
Polyethylene-polyethylene	Intermediate	Intermediate
Polyester-polyester	Rapid	Intermediate
Tenite Acetate-Tenite Acetate	Intermediate	Strong
Tenite Butyrate-Tenite Butyrate	Intermediate	Strong
Metal-cork	Rapid	Strong
Metal-felt	Rapid	Strong
Glass-cork	Rapid	Strong
Glass-felt	Rapid	Strong
Wood-wood (maple)	Intermediate	Strong
Metal-leather	Intermediate	Strong
Metal-rubber	Rapid	Strong
Rubber-rubber	Rapid	Strong
Rubber-cardboard	Rapid	Strong
Glass-steel	Intermediate	Strong
Nylon-nylon	Rapid	Intermediate
Glass-Tenite Butyrate	Intermediate	Intermediate

[a] Rapid denotes bond-setting within 1 minute; intermediate, within 1 to 3 minutes; slow, after 3 minutes. [b] Bonds of intermediate strength could be peeled apart without breaking the adherends. Data in this column are qualitative.

lustrate the adhesive properties exhibited by this class of compounds. *Bonding Speed and Strengths Using Various Adherends.*—The adherend combinations listed in Table I were bonded successfully with methyl 2-cyanoacrylate adhesive. Setting occurred within a few seconds to a few minutes after the parts were joined properly; for example, glass-glass bonds normally set within 10 seconds, wood-wood (kiln-dried maple) bonds within 3 minutes, and steel-steel bonds within 2 minutes. Setting time varied with the inhibitor content and the viscosity of the adhesive, the nature of the adherends, the temperature, and the humidity. Certain thin plastic films bonded together showed good tensile properties but exhibited less strength under a stripping action. Bonded acetate film had good resistance to both peeling and stripping action. On the other hand, bonded pieces of Mylar polyester film had good tensile properties but could be peeled apart with relative ease. Apparently, there are few materials which do not bond to some extent with alkyl 2-cyanoacrylate adhesives.

TABLE III

Shear Strength of Stainless Steel-Stainless Steel[a] Bonds Produced with Methyl 2-Cyanoacrylate Adhesive

Curing Time at Room Temperature, hr.	Shear Strength, psi.
24	1735
40	1775

[a] Surfaces milled.

TABLE II

Tensile Strength of Steel-Steel Bonds Produced With Methyl 2-Cyanoacrylate Adhesive and Cured at Room Temperature

Curing Time	Tensile Strength, psi
2 hr.	2005
4 hr.	2605
22 hr	3110
24 hr.	3840
48 hr.	5030
1 wk.	4895
4 wk.	4030
4 mo.	3960

Methyl 2-cyanoacrylate adhesive forms strong bonds almost immediately with steel specimens. The results presented in Table II indicate that, when the adhesive is cured at room temperature, maximum bond strength is attained after about 48 hours. Bonded articles can be handled, however, within minutes after the bond is formed. Only slight reduction in bond strength occurred in specimens aged for 4 months. In certain applications, use of small amounts of weakly basic substances as bonding accelerators may be advisable to insure rapid development of a high tensile strength.

Shear strengths of bonded stainless steel specimens are recorded in Table III. These values are considerably less than those recorded for tensile strengths. *Resistance of Bonds to Heat, Chemicals, and Weathering.*—Bonds formed with methyl 2-cyanoacrylate adhesive exhibit good resistance to heat. For example, bonded steel specimens were resistant to a temperature of 120°C for periods up to 24 hours (see Table IV), and bonds cured for 5 days at room temperature had a tensile

TABLE IV

Effect of Heat on Steel-Steel Bonds Produced With Methyl 2-Cyanoacrylate Adhesive

Curing Time at Room Temperature	Heating Conditions Temp., °C	Time	Tensile Strength, psi[a]
25 hr.	70	4 days	8400
24 hr.	70	1 wk.	8900
24 hr.	70	10 days	8500
24 hr.	80	24 hr.	8400
24 hr.	120	24 hr.	3400
5 days	140-145	4 hr.	3620
3 min.	260	5 min.	330
3 min.	260	10 min.	360
24 hr.	-17	24 hr.	4620

[a] Tensile test run at room temperature.

strength of 3620 psi after 4 hours at 140-145°C. The cured adhesive bond has a softening point of approximately 165°C and the bond strength, of course, is governed by this value. As shown in Table IV, specimens which had been subjected to temperatures of 260°C showed bond strengths above psi on cooling. The bond strength obtained is probably that resulting from melting the polymer between the test specimens and allowing it to resolidify.

Temperatures up to 80°C considerably strengthen the bond between steel specimens. As indicated in Table IV, a maximum strength of 8900 psi was recorded for a bond cured for 24 hours at room temperature and then held for 1 week at 70°C.

Excellent properties at low temperature were shown by bonds prepared with methyl 2-cyanoacrylate adhesive; for example, bonds aged 24 hours at −17°C retained their initial high tensile strength (Table IV). Qualitative examination of bonded specimens cooled in dry ice for several hours revealed no observable deterioration in the quality of aluminum-aluminum and glass-glass bonds.

The data in Table V indicate that bonded steel specimens offer excellent resistance to most common organic solvents, such as benzene, acetone, and ethyl alcohol. However, the bond was gradually dissolved by N, N-dimethylformamide. Bonds immersed in dilute alkali were weakened noticeably, but dilute acid had less effect. At room temperature, water exerted a moderate weakening effect on bond strength. Steam at 100°C reduced the bond strength to 150 psi. Bonded specimens exposed to water or steam regained a portion of their strength when cured for several days at room temperature.

Bonded specimens are resistant to common industrial fluids. The data in Table VI indicate that the bonds have excellent resistance to synthetic and natural lubricating oils, gasoline, hydraulic brake fluid, and plasticizers.

Proper curing of bonded steel specimens has a profound influence on bonds exposed to high humidity. The data in Table VII show that tensile specimens exposed to high humidity at room temperature suffer some reduction in tensile strength. Bonds with excellent resistance to high humidity at 100°F were produced by curing for 24 hours at room temperature and then for 24 hours at 70°C. It is noteworthy that bonds exposed to high humidity at 100°F for 48 hours followed by 24 hours' curing at 70°C (dry heat) were greatly strengthened. Although no explanation for these phenomena has been found, a comparison of experiments 7, 8, and 9 in Table VII indicates that the increased strengths noted for the sample of experiments 7 and 8 could be the result of a drying process. On the other hand, the relaxation of internal strains at 70°C could be the cause of the increased bond strength noted in experiment 8.

The effect of weathering was examined qualitatively on a number of adherend combinations. Simple lap joints were prepared with the following combinations:

1. Wood (maple) Tenite Butyrate
2. Wood (maple) aluminum
3. Wood-wood (maple)
4. Steel-steel
5. Aluminum-rubber
6. Aluminum-Tenite Butyrate
7. Tenite Butyrate-Tenite Butyrate

The bonds were tested weekly to determine whether failure had occurred. These bonds, with the exception of those involving aluminum, withstood the effects of weathering for 8 months or longer.

TABLE V

Chemical and Solvent Resistance of Steel-Steel Bonds Produced With Methyl 2-Cyanoacrylate Adhesive

Test Conditions[a]			Tensile Strength After Test,
Time of Test, Days	Immersed In	Temp., °C	psi
1	Water	25	2225
1	Water[b]	25	3975
9	Water	25	2455
1	Ethyl alcohol	25	3420
9	Ethyl alcohol	25	4165
1	10% NaOH soln.	25	1680
1	10% HCl soln.	25	3135
1	Acetone	25	4465
1	Benzene	25	4355
1	Water	75	3050
1	Water	100	150
1	Water[c]	100	730
14	N, N-Dimethyl-formamide[d]	25	0

[a] All bonds cured for 1 day at room temperature prior to the tests.
[b] Immersion in water followed by aging for 4 days at room temperature.
[c] Immersion in water followed by aging for 1 day at room temperature.
[d] Bonds cured for 48 hours at room temperature.

EXPERIMENTAL SECTION

Preparation of Adherend Surfaces

All surfaces to be bonded were prepared so that they made smooth, close contact. Wood surfaces were sanded smooth before being bonded, and metal surfaces were freed of loose particles, oil, and dirt. Oxide coatings were removed from aluminum surfaces. Care was taken to exclude acidic and basic substances from the freshly prepared surfaces.

Application of Adhesive

The adhesive was applied with a medicine dropper or a collapsible metal tube. Only one of the surfaces to be bonded was coated with the adhesive. Due to the rapid setting, care was taken to adjust the adherends properly within a few seconds after contact. Manual pressure on the adherends (approximately 10 psi) was usually sufficient to assure a firm bond. The adhesive was applied at the rate of approximately two drops (about 0.06 ml) per square inch for nonporous materials. Porous materials required considerably more adhesive.

Test Procedures

All tensile strengths referred to in this discussion were obtained using the steel-steel specimens described below unless otherwise specified. This type of specimen was used because such bonds were readily prepared and could be subjected easily to the test conditions (heat, cold, action of chemicals, etc.).

Tensile strength values listed in Tables II and IV-VII were obtained using cylindrical steel specimens

TABLE VI

Effect of Industrial Fluids on Steel-Steel Bonds Produced With Methyl 2-Cyanoacrylate Adhesive

Fluid	Tensile Strength, psi[a]
Gasoline	5300
SAE 30 engine oil	4300
Synthetic lube-7808	3600
Dioctyl phthalate	4200
Hydraulic brake fluid	3600

[a] Bonds were cured at room temperature for 48 hours and then immersed in test solvent for 2 weeks at room temperature.

meeting ASTM specifications (ASTM Designation: D897-49). The butt ends of the specimens were ground flat and parallel and each was 1.125" in diameter. After the contact surfaces had been thoroughly cleaned with acetone and carbon tetrachloride, the specimens were joined at the butt ends by means of the adhesive. The only pressure applied was the weight of one test specimen on the other. The bonds were aged for the desired time and then were broken in tension on a Baldwin-Southwark testing machine at a cross-head separation speed of 0.01 ipm.

The shear strength values were obtained according to ASTM Designation: D1002-49T using stainless steel specimens measuring 5 x 1 x 0.064 inches. After the contact surfaces had been thoroughly cleaned with acetone and carbon tetrachloride, the specimens were joined by a lap joint by means of the adhesive. After the desired aging period, the bonds were broken in tension on a Baldwin-Southwark testing machine at a loading rate of 500-700 pounds per minute.

SUMMARY

The discovery of extremely rapid adhesive action of the alkyl 2-cyanoacrylates provides the basis for a new type of solvent-free adhesive. Strong, rapid-setting bonds are formed with a wide variety of adherend combinations. These adhesives function by an anionic polymerization mechanism catalyzed by traces of water or other weak bases present on the adherend surfaces. This polymerization affords a rapid setting action; for example, strong glass-glass bonds are obtained within 10 seconds, steel-steel bonds within 2 minutes, and wood-wood bonds within 3 minutes. These adhesives can function without the use of added catalyst and do not require the use of heat or excessive pressure for development of strong bonds.

Bonds prepared with alkyl 2-cyanoacrylate adhesives have good stability. Bonded articles have good low-temperature properties and good solvent resistance. Bonds withstand moderate temperatures and have good resistance to acids and alkalies. Resistance to actual weathering is good over periods of 8 months or longer.

Adhesives of this type are expected to find their greatest use in household and industrial applications in which their rapid setting action may be used to advantage. The ability to bond a variety of dissimilar materials makes the adhesives suitable for many industrial uses. The rapid setting action makes them particularly useful in the assembly of complicated instruments and electronic devices. The combination of the rapid setting action and high bond strength differentiates these adhesives from other industrial bonding materials and will permit the use of new cost-saving methods in assembly operations.

TABLE VII

Weathering Properties of Steel-Steel Bonds Produced With Methyl 2-Cyanoacrylate Adhesive

Expt. No.	Room Temp. Cure Time Prior to Tests, hr	Weathering Time, days	Temp. at 93 ± 2% Humidity, °F	Tensile Strength After Test, psi
1	24	8	77	2735
2	0	2	100	3090
3	24	4	100	2670
4	24	7	100	2390
5	24	19	100	1805
6	24	28	100	1150
7	48	13	100[a]	4440
8	48	14	100[b]	6295
9	48	15	100	3830
10	24[c]	5	100	4405

[a] Weathering test followed by aging for 2 days at room temperature.
[b] Weathering test followed by aging for 24 hr. at 70°C (dry heat).
[c] Followed by 24 hr. at 70°C.

Acknowledgment

The authors gratefully acknowledge the bond-strength data supplied by Dr. Paul Von Bramer, of Eastman Chemical Products, Inc.

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Leonard F. Sansone, Jr., attended Carnegie Institute of Technology and received a B.S. Degree in Engineering in 1951. First employed as a process engineer by United States Steel Central Operations, he transferred to National Tube in 1952. Having assisted in the initiation of plastic pipe production at Gary, Indiana in 1954, he is presently engaged in resin evaluation, process development, and in the preparation of plastics technical service data. A member of the ASME and the Society of Rheology, he is also active in various committees of the SPI, ASA, and ASTM.

Leonard F. Sansone, Jr.

A Comparison of Short-Time Versus Long-Time Properties of Plastic Pipe Under Hydrostatic Pressure

Leonard F. Sansone, Jr.
National Tube Division
United States Steel Corporation

IN EVALUATING the suitability of a thermoplastic resin for use in pipe, certain properties are of primary importance. Among these are tensile strength, elastic modulus, impact strength, and chemical resistance. For rigid pipe, it is desirable to have all these properties high; but for flexible pipe, we must accept a lower tensile strength in order to achieve a low elastic modulus. Other considerations in choosing a resin include extrudability and ease of joining.

These properties are readily determined and resins which appear suitable for pipe may be easily chosen. However, it is not possible to determine the proper pressure rating for a pipe of certain dimensions based on these properties, since plastic materials undergo creep deformation even at temperatures below room temperature. In general, we expect a material to have good long-term properties if it has high tensile strength and retains a high proportion of its room temperature strength at higher temperatures. This is a good basis for selecting resins for further study, but it is not possible to arrive at suitable working stresses based on the short-term tensile properties.

In order to determine suitable working stresses for pipe, it is necessary to conduct a testing program which involves pressuring pipe samples at various pressures and temperatures for extended periods of time. Depending on the physical conditions and the type of resin, various types of failures are observed. Ductile or brittle rupture, weeping or excessive creep may determine failure.

The essential information which we desire from long-term pressure testing is the relationship between working stress and temperature. To achieve this it is necessary to determine the type of failure encountered and to determine what constitutes a satisfactory service life. In order to compare the four materials to be discussed, a service life of 100,000 hours (11.4 years) has been assumed. This life may be satisfactory in certain applications such as those where alternate materials have shorter life due to corrosion, but may be too short for others. From the data presented, it is possible to determine working stresses for longer service lives so that the designer may choose the service life which he feels is necessary for his application.

0.945 Density Polyethylene

Fig. 1 shows the results of short-term burst tests conducted at various temperatures under conditions specified in ASTM Test Method D-1599-58T. The tests were performed on 1" nominal diameter pipe produced from 0.945 density Ziegler-type linear polyethylene. In order to reduce the burst pressure values to unit stresses,

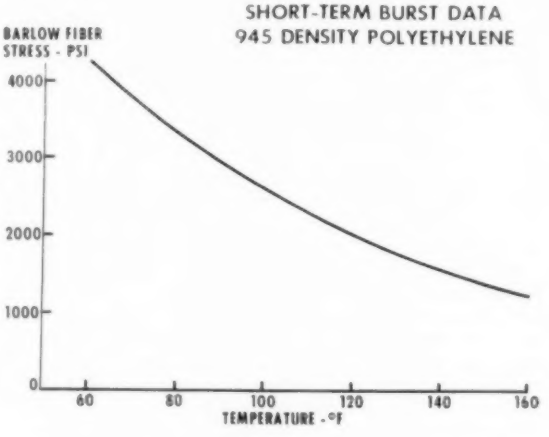

Figure 1.

the Barlow formula was used. This formula has the form:

$$f = \frac{PD}{2t_w} \text{ where } f = \text{unit}$$

fiber stress, P = burst pressure, D = average outside diameter, and t_w = minimum wall thickness (Ref. 1). The fiber stress at burst is comparable to the tensile strength of the material, although it does not correlate completely due to rate effects in testing. Also, the stress in the pipe wall is not uniform throughout the wall thickness.

It is noted that temperature has a marked effect on the burst fiber stress, the stress dropping from 3500 psi at 75°F to less than half that value at 160°F. As will be shown, this is typical for thermoplastic materials.

If the long-term properties of a material were not known, a first approach in determining suitable working stresses might be to utilize a given fraction of the short-term strength. This approach works well with steels in the lower temperature range, but when temperatures 900°F and up are encountered, working stresses must be determined from creep considerations. It has been found that thermoplastic materials in their useful temperature range behave similarly to steels in the upper temperature range. Therefore, tests over extended periods of time are required to determine the long-term strength of thermoplastic materials.

Fig. 2 shows the results of long-term hydrostatic pressure tests at various temperatures on 0.945 density polyethylene. The data was published by Hercules Powder Company (Ref. 1) and is based on original work performed by Dr. K. Richard (Ref. 2) on Ziegler polyethylene in Germany. A plot of the logarithm of the Barlow fiber stress versus the logarithm of the minimum time to failure yields a linear relationship with moderate slope in the initial portion of the curve. In this portion the pipe fails in a ductile manner forming a bubble which finally ruptures. At later times the slope of the curve becomes much steeper and the pipe fails in a brittle manner by forming cracks or pinholes at low extensions. As shown by the curves, the time to the start of brittle failure is displaced to a shorter time by increased temperature. At 176°F only about 1,000 hours are required to determine the shape of the curve, while 10,000 hours are required to determine the shape at 122°F. This points out the value of testing at temperatures higher than the maximum useful temperature in order to determine quickly the characteristic shape of the failure curve.

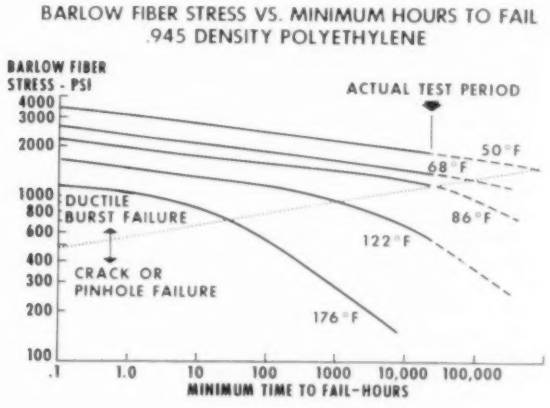

Figure 2.

Since the curves are parallel and the locus of the knees can be predicted by extrapolation, predictions of minimum failure times can be made. If a minimum service life is chosen, the suitable stress for each temperature may be found at the intersection of the minimum failure time and the curve for each temperature. Fig. 3 shows a plot of Barlow fiber stress versus temperature which was obtained in this manner. As stated before, the service life chosen was 100,000 hours which may or may not be satisfactory depending upon the particular application. Similar curves may readily be developed for longer times by referring back to Fig. 2.

The question arises, "Can the stress-temperature curve shown in Fig. 3 be used directly to pressure-rate pipe?" Since the curves in Fig. 2 from which the stress relationship was derived are statistically determined on the basis of minimum time to failure, we would expect very few failures at times less than 100,000 hours provided the pipe was exposed to the same environment used in the tests. However, pipe in use is exposed to a variety of stresses due to earth-loading, bending stresses, and thermal expansion and contraction. In addition, the pipe may be abraded during installation reducing the effective wall thickness by 0.005" or 0.010". Although these factors are not great, some allowance for them should be made. It is impossible to assign an exact value to these other factors since they vary so widely. Looking at the German practice

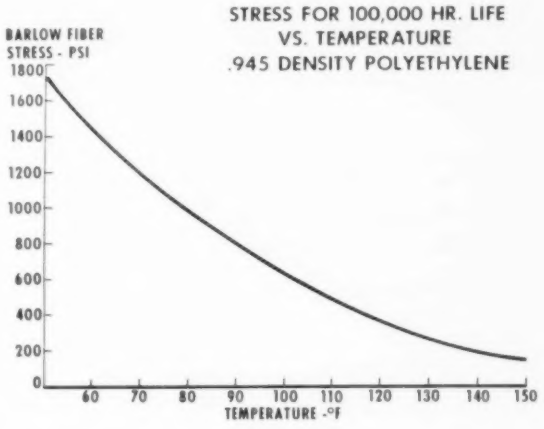

Figure 3.

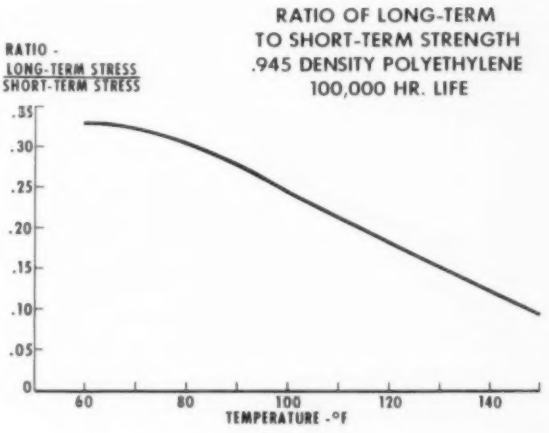

Figure 4.

where a service life of 50 years is required by the water works authorities, the approach has been to divide the allowable stress for 50 years minimum life by a factor of 1.3 (at 68°F). This is reasonable since it allows for 30% additional stress due to indeterminate factors.

In applying a factor of 1.3 to the 100,000-hour allowable stress at 68°F, the minimum life is extended to 600,000 hours. Indeterminate factors which increase the stress level would then cause the pipe to fail between 100,000 and 600,000 hours so long as the stress level was not raised more than 30%.

Fig. 4 shows a comparison of the long-term and short-term strength with respect to temperature. At 75°F the long-term strength is about 31% of the short-term strength, and this value drops off to about 9% at 150°F. Suppose we had not recognized the creep-rupture properties of polyethylene and had arbitrarily used a value of 20% of the short-term strength derived from Fig. 1. At temperatures below 115°F the stress values would be conservative, while at temperatures higher than 115°F they would be much too high. This points out the need for long-term testing so that a material may be effectively utilized throughout its useful temperature range.

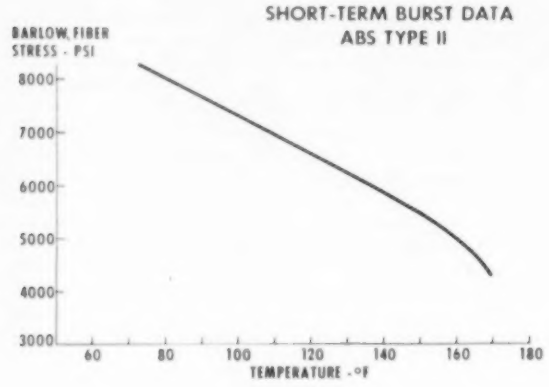

Figure 5.

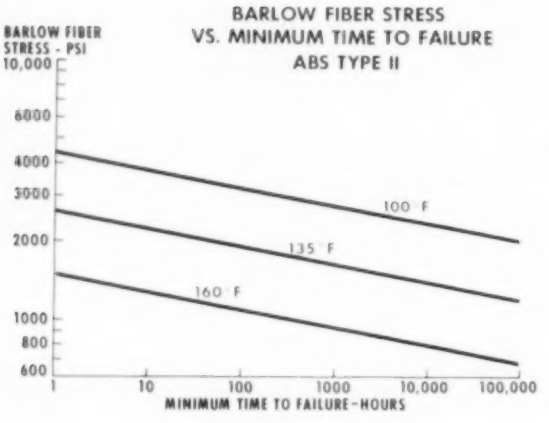

Figure 6.

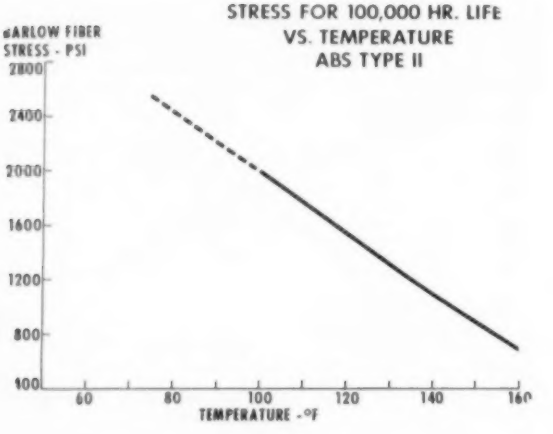

Figure 7.

ABS Type II

A new type ABS (acrylonitrile-butadiene-styrene) polymer which has a tensile strength of about 7500 psi at 75°F was recently introduced. The material has good impact strength, stiffness and chemical resistance and shows promise for general piping applications as well as for special corrosion-resistant applications.

Fig. 5 shows a plot of short-term burst strength versus temperature. The curve is somewhat unusual in that it becomes concave downward at about 150°F, whereas most thermoplastic materials are characterized by a concave upward curve. Data concerning the tensile strength shows a similar curve in the range of temperature shown, but at about 200°F a point of inflection is reached and the curve becomes concave upward at higher temperatures.

Minimum failure time for pipe samples pressured hydrostatically at various stresses and temperatures are indicated by the curves shown in Fig. 6. The lines are linear, parallel, and displaced downward by increased temperature when the data is plotted on log-log coordinates. Due to experience with polyethylene, the possibility of encountering a knee in the curve arises. However, work with a variety of thermoplastic materials indicates that only crystalline materials are subject to the ductile-brittle transition. Since ABS Type II is not crystalline, no knee is expected. The low extension noted, less than 5% even at early failure times, indicates that the material is essentially failing in a brittle manner. The samples show only longitudinal cracks and do not show bubble formation, a characteristic of early failures with polyethylene. This additional evidence leads us to believe that the failure curves for ABS Type II are of the same nature as the second portion of the curves for polyethylene. It is therefore valid to extrapolate the curves to longer times on a linear logarithmic basis. The degree of accuracy is dependent upon taking a sufficient number of random samples from several production lots representative of production variation. Also, longer testing times provide greater accuracy in extrapolating to a given service life.

For the purpose of estimating the stresses suitable at various temperatures to provide 100,000 hours service life, the curves have been extrapolated to 100,000 hours. Since the curves are based on 2,000-hour data, the values arrived at for 100,000 hours are not too reliable. It has been shown that an extrapolation of one log cycle gives valid results at the present time and that there is a possibility of extending this to more than one cycle as testing procedures are refined and

more is learned about the behavior of various classes of thermoplastic resins.

The estimated stresses to provide a service life of 100,000 hours at various temperatures are indicated in Fig. 7. In order to make an allowance for the fact that the slope of the failure curves is not accurately known, it is suggested that the stress values shown in Fig. 7 be divided by a factor of 1.75. Since the slope of the failure curves is small, this has the effect of moving the predicted minimum failure time out to about 10^9 hours or about 100,000 years. As more data is collected and points on the failure curve at longer times are added, extrapolation will become more accurate and it will be possible to reduce the factor from 1.75 to some lower value.

Fig. 8 shows the ratio of long-term to short-term strength at various temperatures. As with polyethylene, the long-term strength becomes a significantly smaller portion of the short-term strength as the temperature is increased. This again points out the inadequacy of short-term data in determining suitable rating stresses for thermoplastic materials.

PVC Type II

Polyvinyl chloride (PVC) normally has an Izod impact strength of about 0.8 to 1.0 foot-pound per inch of notch at 75°F and may be too brittle for certain applications where rough handling is encountered. In order to improve the impact strength PVC Type II was developed. The addition of a rubber copolymer improves the impact strength while reducing the tensile strength, stiffness, chemical resistance, and long-term strength. However, the physical properties after modification are still quite good, and PVC Type II has found wide application in chemical plants, the oil fields, paper mills, and many other industries.

Short-term burst fiber stresses at various temperatures are shown for PVC Type II in Fig. 9. The curve is similar to that for PVC Type I except that it is displaced downward, reflecting the loss in short-term strength due to rubber modification. Short-term burst samples show a significant amount of swelling, as much as 10% or 20% at the higher temperatures and a characteristic longitudinal crack.

When the stress is reduced below the short-term value and the pipe held under hydrostatic pressure for long periods of time, a different mode of failure is noted. After about 0.4% to 2.5% circumferential creep expansion, the material becomes porous at weld lines formed by the breaker plate and mandrel spider. This allows the water to flow out slowly through the porous structure causing droplets to form which have the appearance of condensation. This type of failure has been described as "weeping" and has been observed in other materials, particularly blends of rubber and thermoplastic resins. Surprisingly, the pipe does not burst until an elasped time 2 to 3 times greater than that when weeping is first noted.

The cracks formed are microscopic in size, but their presence may be determined by the appearance of strain whitening, droplet formation if the atmospheric humidity is high, or the appearance of salts and minerals contained in the water together with a drop in the sample temperature if the atmospheric humidity is low. The cracks are so small that if a dye is dissolved in the water it will not pass through the porous structure and the droplets formed on the outside of the pipe will be clear.

The minimum failure time based on weeping at various stress levels is shown in Fig. 10. The curves are quite similar to those for ABS Type II, but are displaced downward for the same temperature and have a steeper slope.

Since the curves are based on 5,000-hour data, they may be reliably extrapolated to 50,000 hours. For purposes of estimating the allowable stress, the curves have been extrapolated to 100,000 hours and the stress

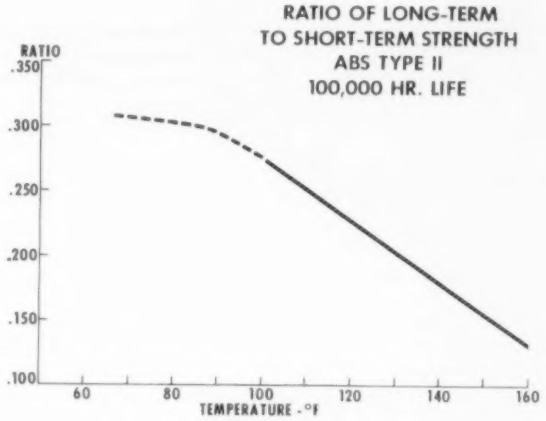

Figure 8.

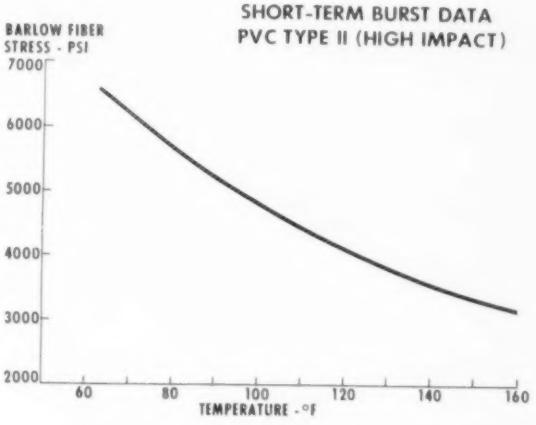

Figure 9.

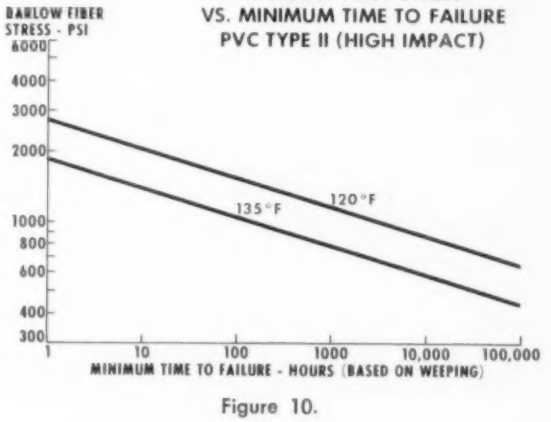

Figure 10.

values plotted in Fig. 11. To arrive at a design stress, division by a factor of 1.5 would be reasonable. This corresponds to a predicted life of 3 million hours or about 340 years by extension of the curves in Fig. 10 to the reduced stress values. Of course these predicted life figures cannot be taken literally due to the excessively large extrapolation used to determine them, but they do serve to illustrate the effect of a reduction of stress on the service life.

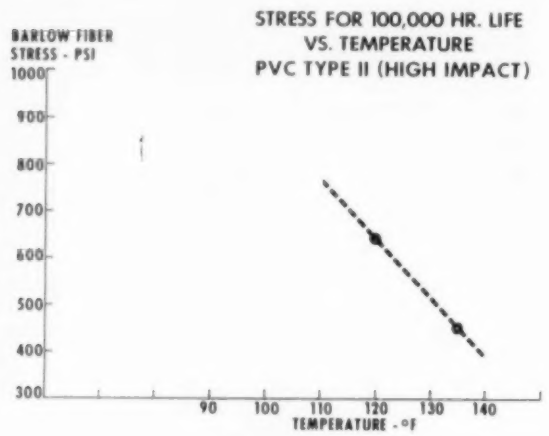

Figure 11.

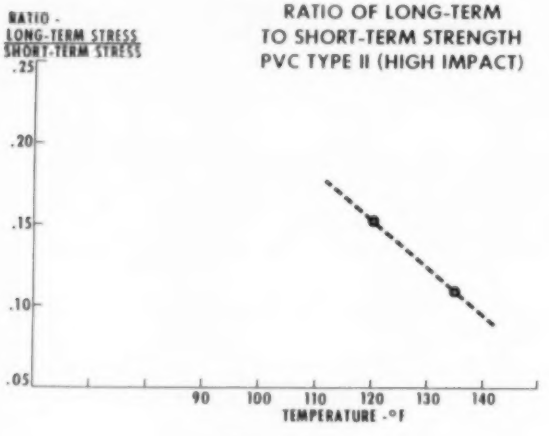

Figure 12.

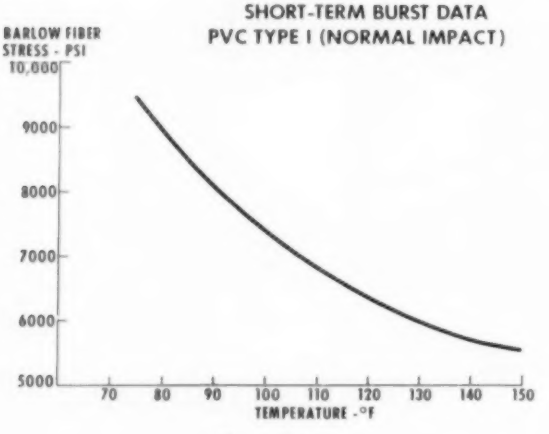

Figure 13.

Fig. 12 shows how the ratio of the long-term to short-term strength of PVC Type II falls off with increased temperature. At 120°F the long-term strength is about 16% that of the short-term, while at 135°F it drops to about 11%. This shows a similar relationship noted with polyethylene and ABS Type II.

PVC Type I

As indicated previously, unmodified or normal-impact polyvinyl chloride (PVC Type I) has excellent tensile strength, stiffness, and chemical resistance but is somewhat deficient in Izod impact strength, having a value of about 0.8 to 1.0 foot-pounds per inch of notch at 75°F. A great amount of PVC Type I has been utilized for several years in applications where PVC Type II is not suitable because of requirements for higher working pressures, higher temperatures, or better chemical resistance. A remarkable small amount of pipe has failed due to impact during shipment, installation, or in service. This is in part due to the availability of high-impact PVC which is recommended for applications at lower temperatures and where rough handling is encountered.

The short-term fiber stress values are shown for PVC Type I in Fig. 13. Short-term burst failures are characterized by brittle failure and sometimes shattering at room temperature and lower, while at higher temperatures appreciable swelling will be noted before rupture.

Pipe samples hydrostatically pressured at 135°F to cause fiber stresses below the short-term value so that failure occurs in less than 20 hours show 1.6% to 4.0% creep extension at rupture. As the stress values are decreased so that failure times become longer, the material exhibits greater creep extension before rupture. When the fiber stress was reduced to 2800 psi at 135°F, extensions at rupture of 6.8% to 20% were noted. A further decrease of the fiber stress to 1790 psi at 135°F showed 7% extension without rupture. The same type of behavior prevails at other temperatures. At fast loading rates, such as in an impact test or short-term burst test, PVC Type I fails in a brittle manner; while at slower rates encountered in long-term creep testing, failure is of a ductile type. Increased temperature has the same effect as increased time in that ductility increases at higher temperatures.

The fact that PVC Type I will expand as much as 20% before rupture precludes the use of a stress rating analysis based on stress-versus-rupture time curves. Threaded joints start to leak at about 10% expansion, so that a pipeline utilizing threaded fittings would have to be repaired long before rupture occurs. Solvent cemented joints can readily withstand 20% expansion, but if it were necessary to install a branch line or if the pipe were moved to a new location, it would not be possible to join the pipe if it had expanded 10% or 15%. For this reason, it is necessary to base the service life of the material on an allowable strain which is less than that to cause rupture and is also less than the amount which will cause threaded joints to leak, or will prevent reassembly with standard fittings.

A detailed study of the relationship between creep strain, time, stress, and temperature for PVC Type I was made utilizing the equipment and method described in the Appendix. Fig. 14 shows the relationship between creep strain and time for the given stresses and temperatures. Similar curves were obtained for uniaxially stressed tensile bars for linear polyethylene by Richard

(Ref. 2) and for branched polyethylene, polychlorotrifluoroethylene, and PVC Type I by Findley and Khosla (Ref. 3). In referring to Fig. 14 it is noted that the curves become linear and nearly parallel after 100 hours with the exception of the one at 2140 psi and 135°F, which shows rupture at 1400 hours after 23% creep extension. The existence of a critical stress level, which if exceeded results in an extremely high creep rate, has been demonstrated for linear polyethylene and polychlorotrifluoroethylene. Richard (Ref. 2) shows the critical stress level to be between 1420 psi and 1700 psi for linear polyethylene at 68°F. Findley and Khosla (Ref. 3) showed a similar behavior for polychlorotrifluorethylene somewhere between 2700 psi and 3600 psi at 77°F, while their data for PVC Type I showed no indication of the critical stress level at stresses up to 4000 psi at 77°F.

Stress levels below these values do not necessarily represent safe stresses since relatively fast creep rates prevail at the higher stress levels just below the critical stress level. Stresses below the critical stress represent an area where the data can be treated by a uniform mathematical analysis in order to determine stress ratings.

By a method similar to one utilized by Findley and Khosla (Ref. 3) the data after 100 hours may be shown to be represented approximately by the equation:

$$s_c = kt^b e^{\frac{-2.3C}{T}} \sinh nf \qquad \text{(Eq. 2)}$$

Symbol		Quantity	Units
where: s_c	=	Creep Strain	%
t	=	Time	Hours
T	=	Absolute Temperature	Deg. Rankine
f	=	Barlow Fiber Stress	psi
k	=	Rate Constant	%
b	=	Logarithmic Slope of Creep Strain - - Time Curve	- -
e	=	Base of Natural Logarithms	- -
C	=	Constant Proportional to the Energy of Activation for Creep	$\frac{1}{°R}$
n	=	Stress Function Constant	$\frac{1}{psi}$

A plot of log creep strain versus log time based on this equation for various temperatures and stresses yields linear parallel curves. However, the data shows a departure from the parallel behavior at the higher strain levels. This is readily explained by the fact that a constant pressure test results in an increase in fiber stress as creep progresses. Realizing that wall thickness of the pipe decreases as the diameter increases, it can be shown that the fiber stress after a given amount of creep becomes approximately:

$$f' = \frac{PD}{2t_w}(1+.02\ s_c) \qquad \text{(Eq. 3)}$$

$$\text{or } f' = f(1+.02\ s_c) \qquad \text{(Eq. 4)}$$

The solution of an exact differential equation yields the relationship:

$$s_c = kt^b e^{\frac{-2.3C}{T}} \sinh nf(1+0.02\ s_c) \qquad \text{(Eq. 5)}$$

No temperature relationship is given in the equation developed by Findley and Khosla (Ref. 3). However, it was shown in an unpublished report (Ref. 4) that the Arrhenius temperature relationship is applicable to creep phenomena observed with PVC Type I.

From the data shown in Fig. 14 the parameters of Eq. 5 were determined to be:

$$b = 0.234$$
$$C = 10{,}950$$
$$k = 6.178 \times 10^{17}$$
$$n = 1.01 \times 10^{-3}$$

In order to construct a stress-versus-temperature curve based on Eq. 5, it is necessary to specify the failure time (100,000 hours) and the allowable creep strain at each temperature. At 150°F the allowable creep strain has been held to 5%, while at lower temperatures the allowable strain has been reduced since rupture may occur at lower strains than 5% in the lower temperature range. Safe strains were chosen based on rupture data and fitted to a curve of log strain

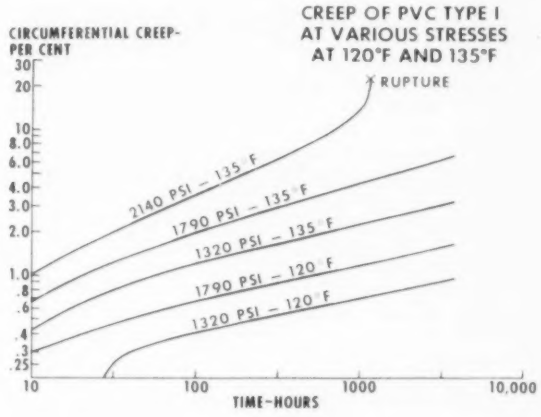

Figure 14.

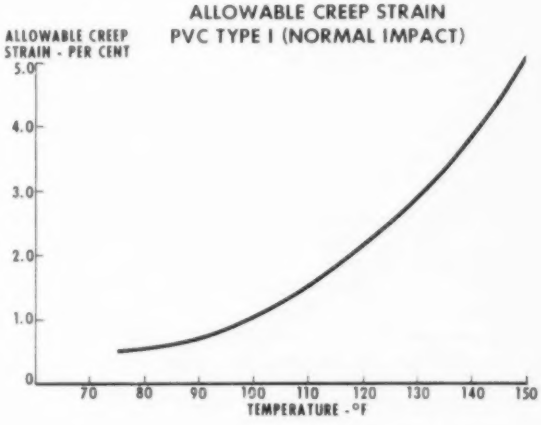

Figure 15.

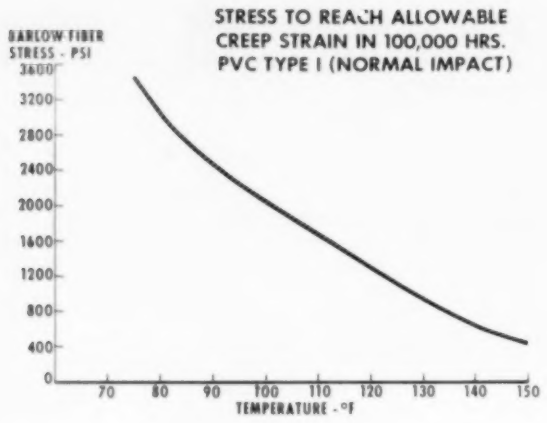

Figure 16.

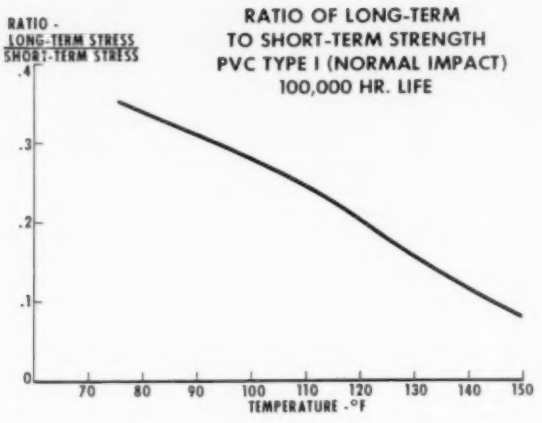

Figure 17.

versus reciprocal absolute temperature, which is shown in linear coordinates in Fig. 15.

The utilization of the allowable strains depicted in Fig. 15 together with Eq. 5 yields the stress rating curve shown in Fig. 16. The stress value at 75°F, 3400 psi, seems rather high, although the stresses at the higher temperatures appear reasonable. Since the data was obtained at 120°F and 135°F, the value at 75°F represents a rather large extrapolation. However, Faupel (Ref. 5) has presented 10,000 hour-stress-rupture data on PVC Type I showing an extrapolated stress value of about 4500 psi for 100,000 hours service life. Until additional data becomes available, published ratings, which are conservative, should be utilized.

Fig. 17 shows the characteristic decrease in the long-term to short-term strength ratio as the temperature is increased. The relationship is quite similar to that observed for the other materials discussed.

Four thermoplastic materials being utilized in pipe have been characterized by the type of failure observed after extended preiods of loading under hydrostatic pressure. Methods of determining rating stresses for extended service periods have been demonstrated for each material. A comparison of the long-term and short-term strength indicates that a rating method based on utilizing a constant percentage of the short-term strength throughout the useful temperature range results in poor utilization of the material at the lower temperatures with a risk of the ratings being too high at the higher temperatures.

Linear polyethylene has been shown to exhibit ductile failure at high stresses and short failure times with a transformation to brittle failure at low stresses and long failure times. Linear polyethylene is amenable to rating methods based on stress-rupture curves provided that the brittle transformation points are located by means of accelerated testing above the maximum useful temperature.

ABS Type II shows essentially brittle failures with less than 5% expansion. Failure may be predicted by stress-rupture methods.

PVC Type II fails by weeping followed by rupture at an elapsed time 2 to 3 times greater than that noted when weeping first occurred. Failure should be defined as the initiation of weeping and may be predicted by stress-rupture curves.

PVC Type I shows brittle failure at short loading times and low temperatures, while at longer loading times and higher temperatures, failure is of a ductile nature with extensions greater than 20% often observed. A method of rating based on creep strain observations is necessary to provide suitable ratings, at least in the higher temperature range. A rating method based on allowable creep strain and an equation relating creep strain, temperature, time and stress has been developed.

Work is continuing to extend the data on present materials to longer times and to provide data over an extended temperature range, as well as to evaluate new resins. The studies of long-term life have resulted in a general classification of thermoplastic resins based on types of failure, thus facilitating the evaluation of new materials which appear to have promise for pipe.

Acknowledgment

The author wishes to express his thanks to J. B. Adamczyk, Junior Metallurgical Research Engineer, and L. J. Lyons, Supervising Chemical Research Engineer, of the National Tube Research Laboratory who were responsible for the design and operation of the creep and stress-rupture equipment. Their help in presenting the data and their description of the equipment found in the appendix is greatly appreciated.

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3. W. N. Findley and Gautam Koshla, "An Equation for Tension Creep of Three Unfilled Thermoplastics," *SPE Journal, XII* (December 1956), pp. 20-25.
4. L. F. Sansone, Jr., Unpublished Report, "Creep Extension of Rigid Polyvinyl Chloride," May 10, 1955.
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APPENDIX

Materials

0.945 Density Polyethylene—Hercules Hi-Fax, Hercules Powder Company, Wilmington, Del.

ABS Type II—Cycolac C, Marbon Chemical Division of Borg-Warner Corporation, Washington, W. Va.

PVC Type I—Geon 8750, B. F. Goodrich Chemical Company, Cleveland, Ohio

PVC Type II—Geon 8700—A, B. F. Goodrich Chemical Company, Cleveland, Ohio

Description of Equipment

The long-term creep and stress-rupture tests on plastic pipe reported in this paper were conducted using equipment which was designed and installed at the Research Laboratory of National Tube Division, United States Steel Corporation. A photograph of the equipment is shown in Fig. 18. The equipment is designed to maintain the sample temperatures within ±2°F with controlled internal hydrostatic pressure. In order to facilitate measurement of circumferential creep, hot air ovens are utilized.

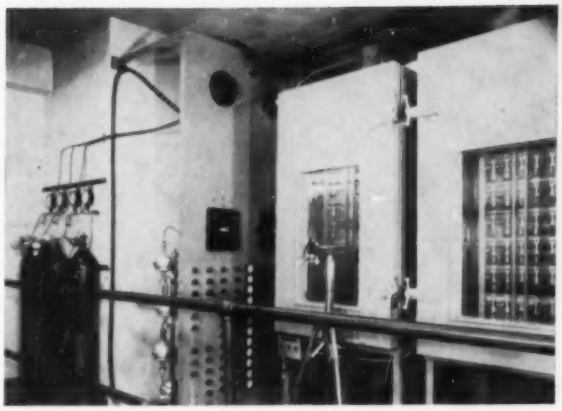

Figure 18. Photograph of equipment for creep testing plastic pipe at research laboratory of National Tube Division, U. S. Steel Corp.

Temperature Control

The ovens shown in Fig. 18 are forced-convection, hot-air ovens, temperature controlled by Weston Celect-Ray potentiometer-type controllers. Four inches of insulation is used throughout except for windows in the front and back doors, which are of double-pane construction.

A Powerstat variable transformer is utilized in a circuit with a relay to provide full current-partial current operation rather than on-off operation of the electric heaters. By means of the Powerstat and a slide resistor, the partial current is set at a level slightly below that required to maintain the desired temperature, while the full current is set slightly above that

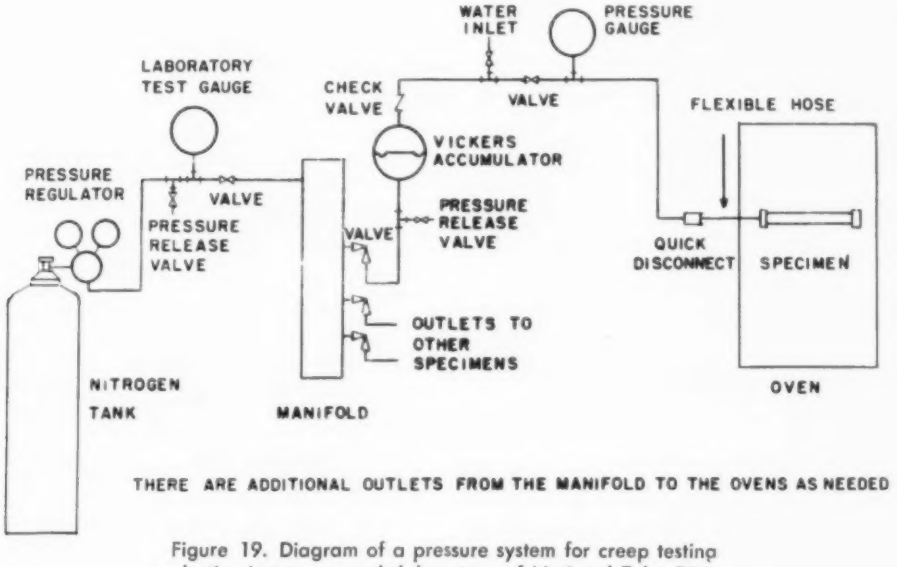

Figure 19. Diagram of a pressure system for creep testing plastic pipe at research laboratory of National Tube Division of U.S. Steel Corp.

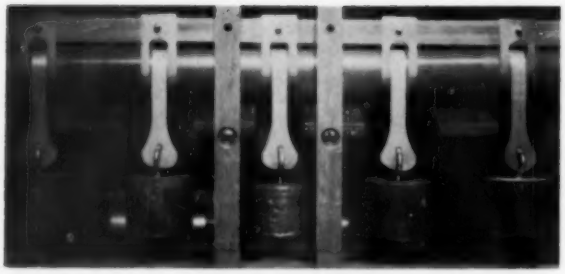

Figure 20. Close-up view of pipe sample with five extensometer strips in place.

level. This circuit provides very stable temperature control since extremes of heat input rate are avoided.

The control thermocouple is located in the center of the oven. Several samples are fitted with internal thermocouples and the sample temperatures, as well as the oven temperatures, are continuously recorded on a single point recorder used in conjunction with a 12-point motor-driven selector switch.

Pressure Control

A typical pressure system used for maintaining constant hydrostatic pressure within the samples is diagrammed in Fig. 19. A nitrogen cylinder with a pressure regulator is used for the constant pressure source and a laboratory test gauge is used to indicate the pressure on the system.

A manifold is used to supply pressure to several accumulators used to transmit the pressure from the gas to the water. The accumulators, which also act as water reservoirs, are Vickers 5″ spherical accumulators containing a neoprene diaphragm.

In order to prevent pressure loss to the other samples pressured through the manifold, a modified check valve closes when one of the samples bursts. A check valve (Circle Seal #259B-2PP) with the spring removed is installed vertically above each accumulator in such a way that the weight of the poppet holds the valve open as long as there is low flow. When a sample bursts the poppet is lifted by the flow surge causing it to seat, thus stopping the flow to the sample and retaining the pressure on the manifold. As a precaution, should the check valve fail, the neoprene diaphragm closes against the water outlet of the accumulator after all the water has been expended. The accumulator and check valve assembly may be seen in Fig. 18.

The water side of the system is fitted with a water inlet valve, a pressure gauge, a quick-disconnect, and a high-pressure flexible hose. The gauge on the water side is used as a check to indicate that the sample is under pressure. This gives assurance that the water in the accumulator has not been expended and that no valves have been inadvertently closed. The flexible hose allows the sample to be filled before placing it in the oven and facilitates its positioning.

Creep Measurements

The samples are placed in an oven on a stainless steel rack, which has six shelves facing each door. These shelves are set at an angle of 12° with the weight of the sample being enough then to hold it against the vertical supports of the rack. Circumferential expansion is measured by extensometers made from 0.002″ thick stainless steel strip, ¾″ wide by 10″ long. Fig. 20 shows a pipe sample in place on the rack with five of these extensometers in place on the sample. As can be seen from the picture, the strips have a slot ⅜″ wide by 1¼″ long near one end, and the other end has been trimmed to a width of 5/16″ so that the strip can be wrapped around the pipe circumferentially and passed through itself. A ⅛″ diameter hole is drilled in each end—at one end for the purpose of hanging the strip on the rack and at the other end for hanging a lead weight on the strip to hold it taut around the sample. As can be seen in Fig. 20, reference marks are scribed on the strip on each side of the section which has been cut out so that they will be at least 10% of the pipe radius above the centerline of the sample when the strip is in place. A series of marks over a length of 1″ and 0.2″ apart are scribed on the reduced section of the strip so that they will fall opposite the reference marks when the strip is wrapped around the sample and looped through itself. Readings are taken by measuring the distance between the reference mark and the 1″ scale mark closest to it, but below it. It is important that the reference mark and the scale mark being read are in the same vertical plane since the readings are taken with a telescope outside the oven. When the sample has expanded enough for the scale mark to move above the reference mark, the next scale mark is used—the distance between the 1″ scale marks being previously accurately calibrated with the telescope.

The telescope used for making these measurements has a magnification of approximately 14.3X and makes use of a Filar eyepiece to determine the distance between marks on the strip. The eyepiece, with a proper lens system, projects an image of a scale and crosshair in the plane of the extensometer strip. The crosshair is moved by means of a micrometer adjustment so that its position may be precisely read. The Filar eyepiece has essentially no play in it and, with this arrangement, measurements can be read accurately to the nearest 0.00025″.

Test Procedure

The test specimens used for this work are 1″ Schedule 80 pipe extruded at the Gary Plastic Pipe Plant of National Tube. The samples are cut 16⅝″ long, and the wall thickness and outside diameter are measured with micrometers, threaded on both ends, and capped. The special caps used are provided with a thick rubber washer which fits inside the end of the pipe within the cap and can be tightened against the inside wall to provide a leakproof seal even after extensive expansion. The sample is filled with water and placed inside the oven with the flexible hose being passed out through a hole in the end wall of the oven which is then filled with asbestos fiber. At least four of the twelve samples in each oven are provided with thermocouples by means of stainless steel protection tubes which extend from one end to the center of the sample. After the five extensometer strips are wrapped around the sample, the quick connect at the end of the flexible hose is connected outside the oven and the sample allowed to set overnight to come up to oven temperature. The next morning the pressure is applied to the sample and readings are taken of the extensometers immediately after applying the pressure. These readings are considered the zero point in determining the creep. All thermal expansion and elastic expansion due to initial pressure application are eliminated by this method.

★ ★ ★

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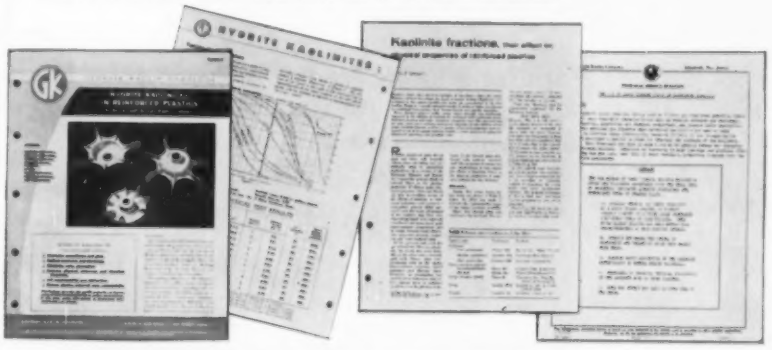

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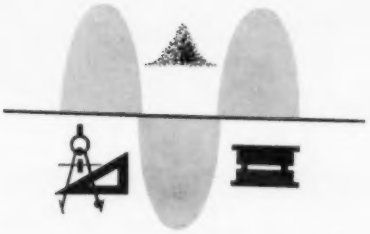

Edited by Louis Paggi, *Consultant*
E. I. du Pont de Nemours & Co., Inc.

FOR AUTHORITATIVE ANSWERS send your questions on molding to Louis Paggi, Sales Service Laboratory, Polychemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington 98, Delaware.

MOLDING CYCLES

ANSWERS TO YOUR MOLDING PROBLEMS:

- *Can a part be molded without stress or strain?*
- *How can you get a distinct grain effect in mottle?*

Q—Is it possible to mold a plastic part free of stress and strain?

A—The subject of stress and strain is an extremely complex one.

If we are thinking in terms of an absolute zero value of stress and strain the answer is "No." It is possible to mold parts in which the stress and strain level is so low as to be tolerable.

The geometry of the part, the type of material used, the method and molding conditions used are all important factors to consider.

For example: A flat disc molded by compression molding may be more stress-free than the same part molded by injection molding. Because of the temperature of the melt used to fill the mold, a deep draw item may be more stress-free when molded by injection molding than by compression. If the same deep draw item is allowed to cool very slowly in the mold the compression molded part may be more stress-free.

Excluding the type of material used, two factors to consider are the energy required to displace material within the mold cavity and the rate of cooling. The greater the energy required to displace material the greater the likelihood of developing stresses. The more rapid the rate of cooling the higher the level of stress developed.

Some of the specific conditions which contribute to a reduction in stresses are:

1. High material temperature
2. High mold temperature
3. Weigh feeding
4. Short ram-in time
5. Short overall cycle
6. Slow cooling
7. Low molding pressure
8. Small gates
9. Flare gates
10. Metal for cavities having low thermal conductivity properties
11. Parts designed with walls of uniform thickness.

The presence of stress (force) always results in strain (deformation). The deformation resulting from stress may or may not be visible. A stretched rubber band is an example of visible strain. An oriented sheet of plastic film is an example of strain which is invisible under normal conditions. In the latter case, the molecules are forced (stressed) into an unnatural position (strained), therefore the structure of the film is deformed not the sheet of film itself.

Warpage in an item may or may not indicate the presence of stress and strain. If the warpage can be eliminated by heating the molded item, the warpage present before heating is visible strain. If warpage occurs as a result of heating, the structure has assumed its natural state, therefore warpage indicates elimination or reduction of stress and strain.

Q—How can I obtain a more distinct grain effect in mottle?

A—The different colors used should have different flow properties. The main or background color should have a softer flow than the graining color. If three colors are used, the two colors used in larger quantity will be of softer flow. In addition to flow properties, it is well to consider the type of coloring material used. Plastics colored by pigments will not intermingle with other colors as will plastics colored with dyes. Lower melt temperatures also tend to minimize blending of colors.

Small gates produce finer graining than large gates. The location of the gate will also influence the general appearance.

Consideration should also be given to the size and design of the heating cylinder. More distinct color separation will be obtained as the capacity of the heating cylinder approaches the shot weight. Molding equipment employing a preplastifying principle will yield inferior color separation.

As a general rule, any condition which tends to improve color dispersion is undesirable for producing mottle effects.

TECHNICAL MEETINGS CALENDAR

16TH ANTEC

ANNUAL TECHNICAL CONFERENCE—January 12-15, 1960, The Conrad Hilton, Chicago, Ill. Sponsored by the Chicago Section. For more information, contact General Chairman Franklin L. Fine, Rohm & Haas Co., 5750 W. Jarvis Ave., Chicago 31, Ill. Request for papers on page 275 of the April SPE Journal.

1959 NATEC

NATIONAL TECHNICAL CONFERENCE—October 13-14, 1959. The Ambassador, Los Angeles, Calif. For more information, contact General Chairman, Jack G. Fuller, % Chemtrol Co. 10872 Stanford Ave., Lynwood, Calif. See tentative program on page 273 of the April SPE Journal.

WORKSHOP

EXTRUSION—June 16 and 17, 1959, Newark College of Engineering, Newark, N. J. Sponsored by Newark Section in cooperation with the Extrusion PAG. Registration is limited to members of the Newark and New York Sections. For more details see page 435 of this issue.

RETECS

PLASTICS IN ELECTRICAL INSULATION—May 22, 1959, Fort Wayne, Ind. Sponsored by the Northern Indiana Section in cooperation with the Plastics in Electrical Insulation PAG. Program includes papers on encapsulation, printed circuitry and fluidized bed coatings. For information write to Chairman Walter A. Gammel, Sr., RBM Controls Div., Essex Wire Corp., Logansport, Ind. For complete program see page 319 of the April SPE Journal.

PLASTICS IN THE AUTOMOTIVE INDUSTRY—June 30, 1959. Sponsored by the Detroit Section in cooperation with the Plastics in the Automotive Industry PAG. For information write to Co-Chairman John Donalds, The Dow Chemical Co., 450 Fisher Bldg., Detroit 2, Mich. For complete program see page 443 of this issue.

VINYL PLASTICS—October 7, 1959, Cleveland, Ohio. Sponsored by the Cleveland Section. For information write to William Messina, 414 Shawnee Place, Huron, Ohio.

PLASTICS FINISHING—October 16, 1959, The Niagara Hotel, Niagara Falls, N. Y. Sponsored by the Buffalo Section in cooperation with the Plastics Finishing PAG. For information write to Chairman Gordon K. Storin, 3 Forest Rd., Lewiston Heights, Lewiston, N. Y.

PLASTICS IN THE SHOE INDUSTRY—November 4, 1959, St. Louis, Mo. Sponsored by the St. Louis Section. For more information write to Otto Wulfert, Chairman, % Wagner Electric Co., 6400 Plymouth Ave., St. Louis 14, Mo.

PLASTICS IN PACKAGING—November 19, 1959, San Francisco, Calif. Sponsored by the Golden Gate Section. For information write to Chairman Frank D. Allen, L. H. Butcher Co., 15th & Vermont Sts., San Francisco 1, Calif.

STABILITY OF PLASTICS—December 1959, Washington, D. C. Sponsored by the Baltimore-Washington Section. For information write to Chairman Myron G. DeFries, Atlantic Research Corp., Alexandria, Va.

SECTION MEETINGS

CHICAGO—May 11, 1959, Western Society of Engineers Building. "Flammability of Plastics," will be the topic of a talk by L. N. Chellis.

CLEVELAND—May 18, 1959, Cleveland Engineering Society, Cleveland, Ohio. "Appliances and Plastics" will be the subject for discussion.

BINGHAMTON—May 23, 1959, Starlight Room, Carlton Hotel, Binghamton, N. Y. The Third Annual Dinner-Dance will feature dinner at 6:30 P.M. and dancing from 9:00 P.M. to 1:00 A.M.

ROCHESTER—May 23, 1959, Rochester Yacht Club, Rochester, N. Y. This Section's Seventh Annual Cruise will start at 6:30 P.M. Program will include cocktails, dinner and entertainment.

PHILADELPHIA—May 26, 1959, Franklin Institute, Philadelphia, Pa. Papers will be presented on the subjects of "Molding Epoxy Resins" and "Precision Injection Molding."

CENTRAL INDIANA—May 26, 1959, Columbia Club, Indianapolis, Ind. This meeting is designated "New Material Night" and will highlight a discussion on Zerlon 150 styrene methyl methacrylate copolymer by B. W. Fay of Dow Chemical Company.

CHICAGO—June 8, 1959, Western Society of Engineers Building, Chicago, Ill. Fred Lauritzen, George's Mfg. Co., will speak on "Guides to Tool Purchasing."

GOLDEN GATE—June 25, 1959. A tour of the Hiller Aircraft plant will be featured. Dinner location to be announced.

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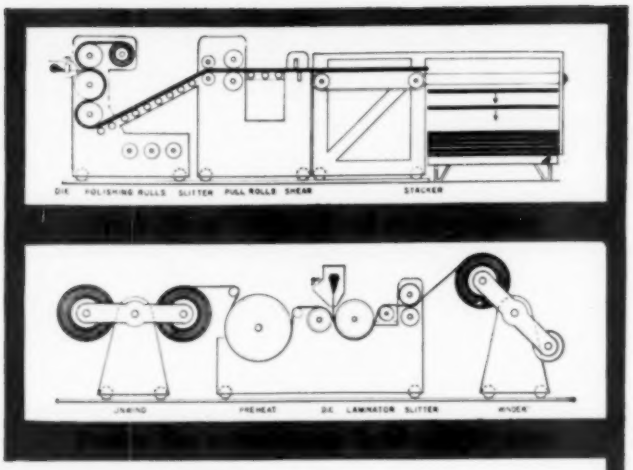

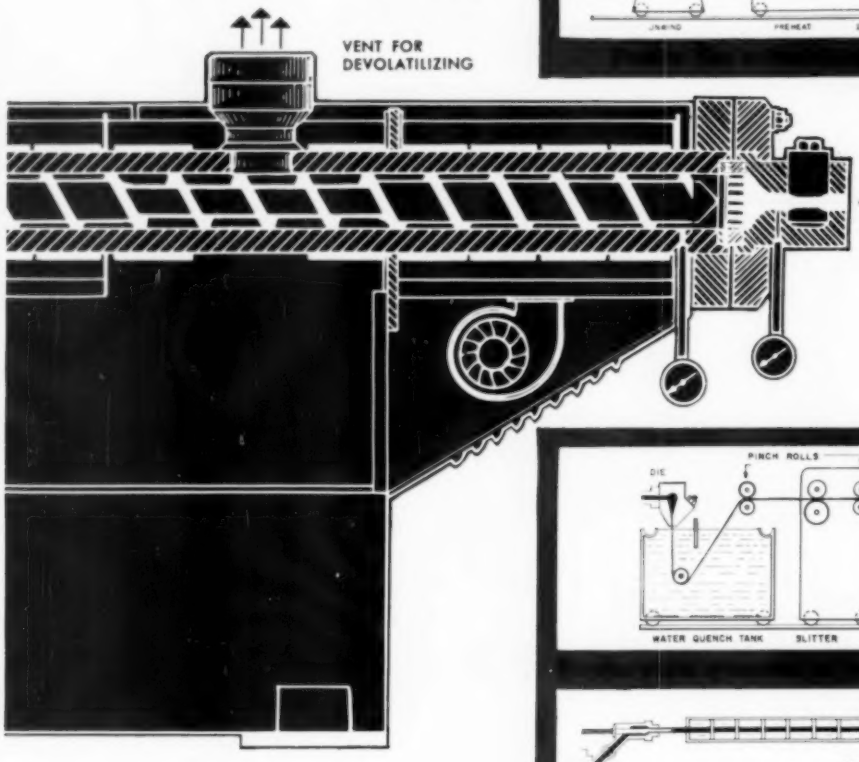

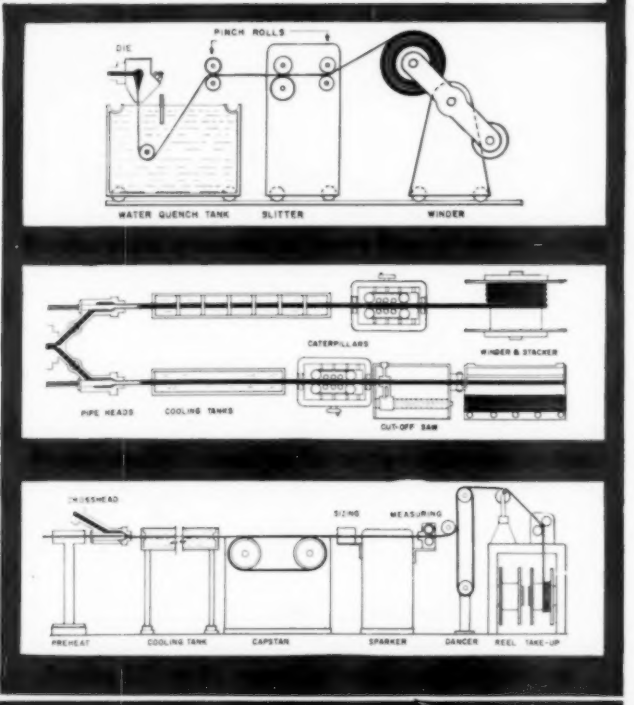

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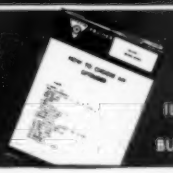

ASK FOR 50 PAGE ILLUSTRATED BULLETIN E-3

Edited by B. H. Maddock
Union Carbide Plastics Co.

SPEAKING of EXTRUSION

Effect of Wear on the Delivery Capacity of Extruder Screws

B. H. Maddock
Union Carbide Plastics Company

Maximum output of a high quality product is always a primary goal of the commercial extruder operator. One of the factors which determines the output rate is the clearance between the screw thread and the barrel. While this factor is negligible in new equipment of proper design, it is a proven fact that screws do wear, with a resultant increase in clearance and decrease in production rate. The rate of wear depends upon the type of material extruded. Hard, abrasive materials or those containing large amounts of abrasive fillers cause wear at a faster rate than the softer plastic materials.

The question, "how much can the clearance be allowed to increase before the screw should be replaced or the flight lands built up?" is one that is frequently asked in the field and one on which there appears to be a variety of opinion. This paper describes a theoretical method for arriving at a practical answer to this question.

It will be recalled (Ref. 1.) that the output rate of an extruder can be described by the equation:

$$Q = \alpha N - (\beta + \gamma)\frac{P}{\eta} \quad \text{(Eq. 1)}$$

Q = open discharge rate—back flow through channel—leakage flow over thread

where:

α = drag flow constant $= \dfrac{\pi D h S \cos^2 \Phi}{2}$

β = back flow constant $= \dfrac{h^3 S \sin\Phi \cos\Phi}{12L}$

γ = leakage flow constant $= \dfrac{\pi^2 D^2 \delta^3 \tan\Phi}{10eL}$

D = barrel diameter
h = channel depth at discharge
S = channel width = lead-thread width
e = thread width
δ = clearance between thread and barrel
Φ = helix angle
L = effective screw length
N = screw speed
P = pressure
η = apparent viscosity in channel

To answer our question we will be interested in the relative magnitudes of the leakage flow over the thread and the back flow through the channel. This can be expressed by the ratio, α/β. Let us also assume a conventional, metering type screw, where:

lead = diameter
thread width = 0.1 x lead = 0.1D
e = 0.1D
channel width = 0.9 x lead = 0.9D
S = 0.9 D

$$\tan\Phi = \frac{1}{\pi} = 0.318$$

$\sin\Phi = 0.303$
$\cos\Phi = 0.953$
$\cos^2\Phi = 0.908$

Substituting these values in the expressions for β and α and taking the ratio of the resultant quantities, we get:

$$\frac{\alpha}{\beta} = 145\left(\frac{\delta}{h}\right)^3 \quad \text{(Eq. 2)}$$

It is noted that this value is independent of screw diameter or length, being a function only of the ratio of clearance to channel depth.

A plot of Eq. 2 is shown in Fig. 1. This plot shows that the leakage flow (α) would be less than 5% of the back flow through the channel (β) if the clearance (δ) were kept under 7% of the channel depth (h). This limit is shown at point A on the graph. It is also seen, point B, that an initial clearance of 5 mils on a screw having a depth of 100 mils would give an insignificant leakage flow of less than 2% of the channel back flow. The leakage increases very rapidly with increasing clearance in a cubical relationship. At a clearance of 10% of the channel depth, point C, the leakage has increased to about 15% of the back flow. The leakage would be 50% of the back flow at δ/h value of 0.15, point D, and equal to the back flow when the clearance reaches about 19% of the channel depth, point E.

A further example in the use of this information is shown in Fig. 2. Line F G H is a calculated screw characteristic curve at 60 rpm for a typical 2½" diameter screw having a channel depth of 0.100" in a 3 turn metering section and an assumed clearance of zero. The calculations are for 0.92 density, 2.0 melt index polyethylene at 190°C. The effect of a clearance of 5 mils ($\delta/h = .05$) or mils ($\delta/h = .10$) is seen to be small and would probably be considered negligible. As the clearance increases still further to 15 and 20 mils or more, the effect can no longer be neglected and one must make a decision as to how great a reduction in output rate can be tolerated before corrective measures are taken. The effect is greater at high pressures or die resistances. With a low resistance die such as shown by the dotted line GJ, the output rate would be reduced about 9% as the clearance was increased by wear to 20 mils. With a higher resistance die, as represented by line HK, the reduction in output rate for the same change in clearance would be 36%.

If we assume an hourly capacity of 100 lbs./hr. for the 2½" machine and a sales markup of 100% of the raw material cost (polyethylene), this machine could be expected to produce at a profit rate of about $20.00/hour. A 15% reduction in yield would thus be equivalent to a loss of $3.00/hour which would

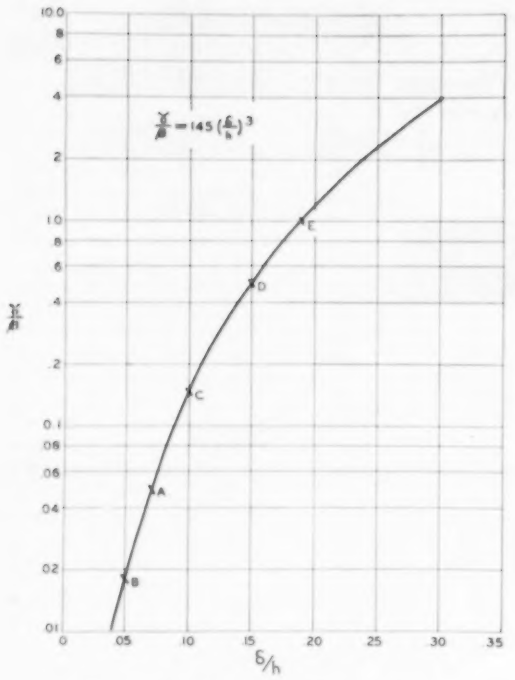

Figure 1. Effect of clearance on leakage flow.

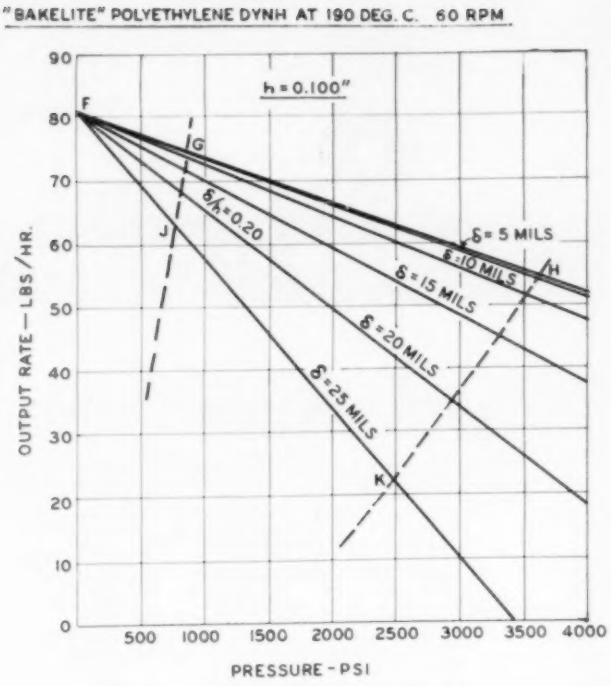

Figure 2. Effect of clearance on output rate of 2.5" metering-type screw.

pay for a new $750.00 screw in about 250 operating hours or for building up the threads of the old screw ($300.00) in about 100 hours.

While each case would have to be determined on its own merits, a reasonable rule-of-thumb would be to specify replacement or repair of a screw when the clearance has increased to about 15% of the channel depth. At this point the leakage flow is equal to about one half of the back flow through the channel or about one-third of the total back flow. Leakage flow is considered negligible if the clearance does not exceed 5.0% of the channel depth at the discharge end of the screw and this value is recommended as a maximum for original screw design.

References

1. Carley, J. F., Mallouk, R. S., and McKelvey, J. M., "Extrusion Symposium", *Ind. Eng. Chem.*, 45, 976 (1953).

★ ★ ★

First SPE Workshop Well Received

Robert D. Sackett
Hartig Extruders

The idea of holding an extrusion workshop was first conceived at the Detroit ANTEC, January, 1958. The Extrusion Professional Activity Group set up a committee headed by R. D. Sackett of Hartig Extruders to study the best means for improving the general technical level of members in the extrusion field. It was the general feeling of the Extrusion PAG that many members were not fully up to date on existing know-how and consequently were not getting full benefit of subsequent talks and publications on extrusion.

Because of the special requirements felt necessary to conduct a satisfactory workshop, an entirely new procedure and technique of conducting an SPE meeting was set up with the approval of the various National Committees concerned. The SPE-PAG Workshop committee set up a curriculum and then selected those people in the industry who were felt best qualified from the standpoint of subject knowledge and ability to instruct others. The classes were set up as nearly as possible to resemble college lecture classes and questions were encouraged at all times. This necessitated restricting the attendance both from the standpoint of number of people that could be handled and to assure that those who did attend would gain sufficiently from the course to justify the time and expense involved. It was suggested that all registrants should have completed courses in College physics and mathematics. In addition, registration was limited to 60 people on a first-come-first-served basis. A registration fee of $25 was charged with the proceeds going to establish a scholarship fund at Lowell Technological Institute in the name of the sponsoring Section, Eastern New England.

The workshop consisted of 12 hours of classroom studies with a two-hour question-and-answer

period in the evening of the first day. The curriculum covered some of the fundamentals of plastic flow and heat transfer in preparation for subsequent discussions on extrusion theory and design. Additional classes were held on quality and power considerations and scaling-up and a theoretical discussion of die design. The problems of extruder instrumentation and take-off as well as basic engineering considerations for extruder design were covered. The following individuals conducted the classes and are to be congratulated for their part in the program. Dr. Ernest Bernhardt and Dr. Heinrich Kessler of DuPont, Bruce Maddock of Union Carbide Plastics, Frank Nissel of Prodex Corp., Murry Underwood of Monsanto, and Earl Veazey of Dow.

A survey of those attending was analyzed as follows: Of the 58 people who filled out questionaires, 13 had taken college graduate studies, 36 additional were college graduates, 7 had completed 2 years of college and 2 were high school graduates. There were 14 people in sales, 20 in engineering, 8 in production, and 15 in research. Approximately 75% felt that the work covered was directed at their technical level with 25% indicating it was over their level but still of value to them. 93% felt that they got from the workshop what they had expected, and there was 100% agreement that a similar workshop should be sponsored in other geographic areas. It is the hope of the Extrusion PAG that further meetings will be possible.

The overwhelming success of the workshop was due in no small part to the general cooperative spirit of all participating parties, SPE Extrusion PAG, Eastern New England Section, Lowell Technological Institute, and the interest exhibited by the registrants.

Pictured are some of the men responsible for the success of the Extrusion Workshop. Top row, left to right: Bruce Maddock, Union Carbide Plastics, *Speaker;* Robert Sackett, Hartig Extruders, *Chairman PAG Extrusion Workshop Committee and Moderator;* Frank Nissell, Prodex Corp., *Speaker;* Heinrich Kessler, DuPont, *Speaker.* Bottom row: Dr. Ernest Bernhardt, DuPont, *Speaker;* Murray Underwood, Monsanto, *Speaker;* Earl Veazey, Dow, *Speaker;* Maynard Axelrod, Maynard Plastics, *Chairman Eastern New England Workshop Committee;* Prof. Russell W. Ehlers, *Representative of Lowell Technological Institute.*

★ ★ ★

Newark Plans Second Extrusion Workshop

Because of the tremendous success of the initial Extrusion Workshop at Lowell Technological Institute, another is presently being planned for June 16-17, 1959, at Newark College of Engineering, Newark, N. J., sponsored jointly by the SPE Extrusion PAG and the SPE Newark section. With the problems of the first Workshop solved, the second should be even more informative.

Many engineers responsible for the profitable operation of extrusion equipment have been unable to keep abreast of the latest technological developments due to the pressure of business. Therefore, the Workshop will consist of a series of informal lectures and discussions of modern extrusion theory and practice with emphasis placed on practical application. The content of the Workshop is aimed at the extrusion engineer with some training in mathematics and physics.

The Workshop will consist of roughly 12 hours of regular classroom studies over a two-day period with a two-hour panel discussion period.

The Extrusion Workshop Committee has selected some of the best extrusion engineering talent available in the industry today to serve as instructors. Each has had a number of years experience and is well versed in the fields they will cover. The lecturers consist of the Moderator: Robert D. Sackett, Hartig Extruders; Dr. Ernest Bernhardt, Du Pont; Bruce Maddock, Union Carbide Plastics; Earl Veazey, Dow Chemical Co.; Murray Underwood, Monsanto Chemical Co.; and Frank Nissel, Prodex Corp. John H. Myers, III of Foster Grant Co., is chairman of the Extrusion PAG, and Robert Sackett is chairman of the Extrusion PAG Workshop Subcommittee.

The Newark Section Workshop Committee consists of Chairman—Bernard Zurkoff, Union Carbide Plastics; Jerry Schaul, Alpha Plastics; Peter Monti, Celanese; Robert Bostwick, Union Carbide Plastics; Len Ryder, Celanese.

Registration will be limited with priority going to members of the Newark and New York Sections. If it is found necessary because of the large number requesting registration, a further priority of one member per company may be instituted. A registration fee of $35 is anticipated. This fee will include coffee breaks, two lunches and one dinner. The proceeds of the Workshop will be used for educational purposes only.

Final details for the Extrusion Workshop are in process. All the information will be in the hands of each member of the Newark and New York SPE Sections by May 1. For any further information, contact Bernard Zurkoff, Union Carbide Plastics Co., Bound Brook, New Jersey.

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ABOUT MEMBERS

Jerome L. Formo, Past National President of SPE and Chairman of the Plastic Study Group of the Building Research Institute, will be among a group of businessmen and Government officials who will soon leave on a Trade Mission to Poland. While in Poland he will visit Warsaw and other important industrial centers, to confer with local business and Government officials.

Mr. Formo is Director of Plastics Research of the Minneapolis Honeywell Regulator Co. He is National Councilman, Upper Midwest Section and Chairman of the Inter-Society Relations Committee. Mr. Formo has been the author of several articles in the plastics field. He is a member also of the Ad Hoc Committee studying the possibility of forming a Plastics Institute.

Jerome L. Formo

Richard M. Weber, Weber Engraving Co., and a Past President of the Golden Gate Section, is reported to be making continuous progress with his health. Strict adherence to doctor's orders gives him the assurance that he will soon be able to resume his SPE activities.

Julius Mate has been appointed technical and sales representative for Western Ohio, Western Pennsylvania and the Western New York area of the National Tool & Manufacturing Co., Kenilworth, N. J. Mr. Mate has been with the Detroit Engineering Co. in a similar capacity for many years. He is a member of the Northwest Pennsylvania Section of SPE.

David L. Sahud, National Secretary of the Polymer Structure and Properties PAG (PSPPAG) and an affiliate of the Newark Section of SPE, has joined the staff of senior scientists at Radiation Applications Inc. of New York. Mr. Sahud, a physical chemist, was formerly employed at Celanese Corporation and did graduate work at Brooklyn Polytechnic Institute.

John H. Myers has joined the staff of Foster Grant Co., in Leominster, Mass., to participate in product development in the capacity of Group Leader. He was formerly associated with the Celanese Corporation of America as Group Leader in polyolefin film extrusion. A graduate of Drexel Institute of Technology and Stevens Institute, Mr. Myers was also professionally affiliated with Monsanto and Bakelite (now Union Carbide Plastics Co.) He is one of the organizers and the current Chairman of the active Extrusion PAG of the SPE, Newark Section and also holds membership in the SPI and A. I. Ch. E.

William F. Brown, of Whitso, Inc., Schiller Park, Ill., was appointed sales manager. He was previously sales manager in charge of injection molding for Chicago Molded Products Corp. Mr. Brown is with the Chicago Section of SPE.

William F. Brown

Hans E. Buecken

Hans E. Buecken, of the Akron Section of SPE, announces the establishment of his own business in Los Angeles as manufacturer's representative and extrusion engineering consultant, to be known as the Hans E. Buecken Company. NRM rubber and plastics extruder sales will be promoted in California, Washington, Oregon, Arizona and Nevada. Mr. Buecken was formerly assistant vice president of National Rubber Machinery Co. He will reside in Santa Barbara, Calif.

Leonard E. Canner of Landers Corp., makers of coated fabrics, was recently promoted to vice president of production. Mr. Canner, who is affiliated with the Toledo Section of SPE, is a graduate of Brown University, and has been with Landers Corp. since 1952.

Herman S. Kaufman, Newark Section has accepted a post as technical assistant to the manager of research at Allied Chemical's central research labs in Morristown, N. J. He was previously supervisor of the polymer properties group at M. W. Kellogg, Inc. Dr. Kaufman, who obtained his PhD at the Polytechnic Institute of Brooklyn in 1947, has published a large number of papers in the field of polymer properties, especially halocarbon polymers. He is a member of the American Chemical Society, American Crystallographic Association, and the Scientific Research Society, and currently holds the position of Vice-Chairman of the newly-formed Polymer Structure and Properties PAG of the SPE.

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George R. Mallory, a member of the Golden Gate Section of SPE, was promoted to vice president of Kimball Mfg. Corp., a division of Bristol Meyers. Mr. Mallory was formerly manufacturing manager, and in his new position he will take complete charge of all production, research, and major purchasing. Kimball specializes in molded reinforced plastics products.

August Napravnik was named production manager in charge of all manufacturing facilities for Catalin Corp. of America, it was announced by Harry Krehbiel, company president. Mr. Napravnik has been associated with Catalin since 1939. His new office will be located at Catalin's Fords, New Jersey plant. He received his Bachelor's degree in chemical engineering and his Master's degree in chemistry at Lehigh University. Affiliated with the Newark Section of SPE, he is also a member of ACS, Chemical Market Research Association and Commercial Chemical Development Association.

Arthur S. Nicholas has formed a new corporation, The Leon Chemical Industries, Inc., with Robert Cox. The main products of this company are acrylic coatings for glass and metals, paint intermediates and formulated epoxy. Mr. Nicholas is president of this company. He is affiliated with the Detroit Section of SPE.

Doyce B. Hanson, manager of technical services for the Plastics Sales Division of Du Pont's Polychemicals Department, has been appointed produce manager in the Department's Research and Development Division. Mr. Hanson is an affiliate of the Philadelphia Section of SPE.

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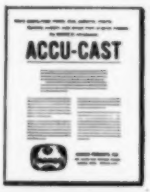

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SECTION NEWS

Central Indiana

Preventive Maintenance of Molding Machines

Wayne Nicely

Sixty-five SPE members and guests gathered at the Warren Hotel on March 31, to hear a panel discussion of "Preventive Maintenance of Molding Machines." Allen Perry of Vickers, Inc. discussed maintenance problems with respect to hydraulic high pressure pumps. The importance of clean oil of the proper type was the subject of a very informative paper by C. L. Middleton of the Socony Mobile Oil Co. Inc. The final presentation was made by Art Evans of Amos Plastics, who outlined a successful organized drive he had conducted to reduce hydraulic oil loss. F. M. Adair of the Western Electric Co. acted as moderator. After the papers were presented, the meeting was opened to questions and discussion.

South Texas

Filler Materials Assayed

Winton B. Adams

During the March meeting at the Houston Engineers and Scientific Societys' Club, Scott Carpenter, sales manager of the White Pigments Dept. of Godfrey L. Cabot Co., spoke on the advantages of developing an informed and accurate analysis for filler materials.

A vote by the Board of Directors decided to present $25.00 to the annual Science Fair sponsored by the Engineering Counsel of Houston for Science students of Houston schools.

Miami Valley

Filled Epoxy Resins

Stephen D. Marcey

Following dinner at the Wishing Well restaurant in Centerville, Ohio, where the April meeting was held, R. T. O'Connor, Devon Corps., was guest speaker. Slides were used to illustrate practical mold applications of epoxy compounds. Several mold samples were on display for the benefit of the members present.

Western New England

Evaluate Extruders

Armand G. Winfield

Evaluation of the extruder as a necessary part of integrated systems of molding, as to the extruder being only a component in a larger scheme of operations rather than the prime unit, was the theme of a talk given by Dr. Ernest C. Bernardt. During the March meeting, Dr. Bernardt, Sales Service Lab., Polychemicals Dept., DuPont, pointed out that interpretation of the defition of extrusion is subjective. He has followed this line and gave a series of his own interpretations as to how the extruder can be used to complement or supplement processes heretofore restricted to less efficient machines. The limitations of injection cylinders are overcome by the even heat distribution of the extruder screw, making it possible to accomplish a wider variety of operations with a selection of "more sophisticated materials." Among the combinations considered were sheet extrusion; sheet forming (vacuum forming, embossing, etc.); blow molding; extruder ram combinations where the melt is fed into a secondary injection system; reciprocating screw operations (primarily a European development which speeds up and improves the extruder-ram process); and finally extrusion-injection (where the extruder acts as the injection unit for low pressure molding on single or turret type multiple mold arrangements). Dr. Bernardt indicated that this conception of the extruder as a component in a machine assembly will bring many expensive optimum performance ranges. The meeting was attended by 86 members.

Binghamton

Educational Problems

Leo J. Pranitis

The February meeting was held at the Castle Restaurant in Scranton, Pa., and was attended by 51 members and guests.

Emery Slaght introduced the speaker of the evening, Mr. Robert Dawson. A graduate of Dickson College, Columbia University, and 20 years in an administrative capacity with the Scranton school system, Mr. Dawson is presently area administrative head for the Pennsylvania State University.

His topic "Current Educational Problems," revealed several incidents he had encountered along this line when he was with the school system and aroused the interest of all present.

Golden Gate

RETEC Committee Changes

Theo. V. Malianni

President Jim Turner opened the March meeting by having Chairman John Bogner introduce and present pins to the following four new members: John J. Joyce, Western Plastics Magazine; Ned L. Roberts, Ned L. Roberts, Inc.; William Stoesser, Stoesser Tool & Die; and Robert Spencer, Varian Associates. It was disclosed that Bill Hodges was forced to resign as

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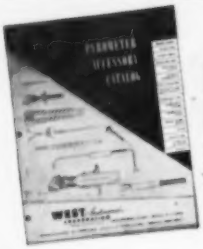

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Treasurer and also as general Chairman of 1959 RETEC, due to other commitments. The following replacements and new committee chairmen are: James C. Smith, Reichhold Chemicals, National Councilman; Bob Wnukowski, Tools, Dies & Molds Co., Treasurer; Frank D. Allen, L. H. Butcher Co., New RETEC General Chairman; Bill Richardson, Rohm & Haas, Program Chairman; Bob Hughes, Industrial Plastics, Editing and Printing Chairman; John Joyce, Western Plastics Magazine, Publicity Chairman; Julius Palen, Lenkurt Electric Co., Co-chairman and Advisor. William F. Christopher, General Electric Company's Chemical Development Department in Pittsfield, Mass., was guest speaker.

St. Louis

Adhesive Bonding

Lyle R. Dean

Guest speaker during the March meeting was John C. Middleton, Supervisor Aircraft Technical Service of the Los Angeles Laboratory for Minnesota Mining and Manufacturing Co. Mr. Middleton explained some of the reasons for the gains made toward accepting adhesive bonds as being: stresses were distributed over the entire surface; mating surfaces had continuous contact; smoother contours were available; flexible joints were possible, and weight savings were possible. He went on to explain that there were two fundamentals to consider in adhesive bonding: (1) the adhesive in a joint must be used to obtain maximum strength, and (2) joints must be designed properly to take advantage of the adhesive. Mr. Middleton went on to explain that there are four types of failures in adhesive joints—tensile, shear, cleavage, and peel. Generally a joint failure will be a combination of one or more of these types.

The different types of adhesives were briefly discussed and broken-down into the two main categories of thermoplastic and thermosetting.

Mr. Middleton concluded his talk by describing the criteria used in selecting adhesives. These are the physical form of the adhesive; the method of application; and the external, exposure, and chemical factors to which the joint will be exposed.

Ontario

Plastics Colorants Trend

Harold A. Shure

Seventy-nine persons attended the March meeting who heard R. J. Frawley, Plastic Color Division, Ferro Corp., Cleveland, Ohio, report on Trends in Colorants for Plastics. As higher molding temperatures become more prevalent in the plastics industy, the need for light fast heat resistant colorants increases. Inorganic pigments of the metallic oxide type can meet these requirements. For a good color match it is advisable for the colorant supplier to be informed which resin is to be used. Properties of a colorant in one plastic are not necessarily the same as its characteristic in another.

During this meeting it was announced that cancellation of the April meeting was necessary because it conflicted with the Canadian SPI annual conference in Montreal.

Newark

Foreign Plastics Field

David Sahud

"Electroforming in Nickel for the Plastics Industry" was the theme of a talk and film rendered by Otto Bohnenberger, President B & E Electroforming, during the March meeting. The technique of electroforming, with particular notice on the importance of carefully controlling the plating bath and the current, was emphasized. The speaker successfully demonstrated the utility of electroforming for producing complex mold cavities and salvaging expensive molds that have developed surface defects. Impressions, made during recent business trips abroad, were given by Joseph Bonanno, Lionel Corp., on the Italian Plastics industry. He stated that due to the rich oil deposits in the Po Valley and Sicily, their major emphasis was on polyolefin and polyvinyl chloride production; their imports of polystyrene (homopolymer and copolymers) and acrylics; their low labor costs resulting in economi-

cal tool production and superior finishing. An observation of Russian interests was spoken of by William Cruse, Executive Vice President of SPI, who was a member of the U. S. Exchange Delegation that toured the Soviet Union several months ago. This 7000 mile tour covered 12 plastics factories.

Southern

Polyethylene Packaging

J. W. Root

Mr. John D. Seay, Jr., chief mechanical engineer, Tenite Development of the Tennessee Eastman Co., Kingsport, Tenn. presented a talk "Progress with Medium Density Polyethylene for Overwrap," which was supplemented by a 20 minute film, "Portrait in Plastics." New developments in the application of polyethylene film in the packaging field were discussed and covered such topics as choice of film material, machinery feeding, and the folding, sealing, and opening of the package.

Recently elected officers were announced as: President—J. B. Williams; Vice President—Clint Griffin; Secretary — William Kelly; Treasurer—W. J. De Brule; National Director—Jules Lindau III.

The regularly scheduled meeting date of the Section has been changed to the fourth Monday of each month.

Chicago

Molding Machines

Harry E. Bennett

Dr. James F. Carley, Engineering Editor of Modern Plastics Magazine, told Chicago's SPE Chapter during the March meeting, that most U. S.-made injection molding machines are inefficient because they rely on heat conduction rather than viscous working to soften the plastic material prior to molding. He explained that all plastics are poor conductors of heat, cannot safely be placed in contact with very hot surfaces, and are too viscous for effective heating by convection. This same high viscosity—about 30,000 times that of water—makes possible very fast, safe and efficient heating of molding resins by viscous working, or shearing and smearing, of the resin. This is accomplished most conveniently in screw extruders, machines whose operation has become much more clearly understood during the last eight years, and which show promise of tremendous increases in productivity in the future. Dr. Carley discussed some new molding machines that use the extrusion-heating principle and presented a short movie showing one of these in action.

Kentuckiana

New ABS Materials Explained

R. O. Carhart

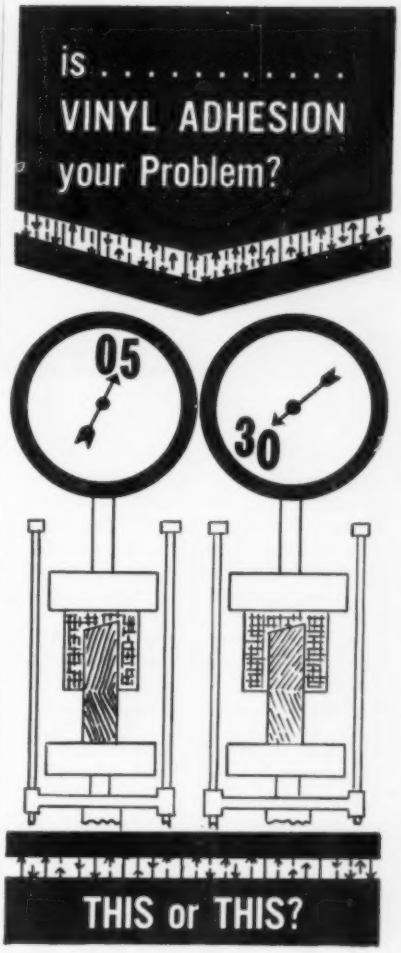
During the March 18th meeting, attended by 26 members and guests, former member K. A. Erwin spoke on "Recent Developments in ABS Materials." The history and application of such materials as well as properties of new formulations that have improved heat and flame resistance, were reviewed. Slides were also used to illustrate this talk. Mr. Erwin is now administrative manager, Research and Development Dept., Marbon Chemical Co. He was also a former member of the Kentuckiana Section.

New York

Highlight Raw Materials

Charles C. Orr

Four speakers, representing major raw material suppliers and processors, addressed the March 18th meeting, held at the Governor Clinton Hotel. It was attended by about 200 members and guests. William E. Rittenhouse, Dow Chemical Co., discussed a "New Copolymer — Methyl Methacrylate-Styrene Compound, Zerlon 150." This thermoplastic handles much like the higher heat resistant polystyrene formulations and can be processed on conventional equipment. The Vinyl Professional Activities Committee heard three papers on pigments. Program moderator Melvin M. Gerson, Sandoz, Inc., discussed requirements of "Pigments for Vinyl Processing." Pigments are preferable to dyes as colorants for vinyls because of their better light-fastness, heat resistance, and lower reactivity with other ingredients used. They must be dispersed



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Members and guests of the Cleveland-Akron Section are shown attending a dinner which succeeded a field trip. On March 9th, a tour of several plants of the Molded Fiber Glass Co., in Ashtabula, Ohio was made, where the group was privileged to observe a variety of polyester applications in authentic production.

properly in order to gain full color value, streak-free colors, and minimum cracking. "Monastral Red and Violet Pigments-Vinyl Applications," were described by Robert H. Zabel, E. I. du Pont de Nemours & Co. Use of azo and non-azo type pigments, especially reds and yellows, is limited because of deficiencies in light-fastness, heat stability, and bleed resistance. L. R. Sherman, Imperial Color Chemical & Paper Corp., spoke on "Selected Inorganic Colorants for Vinyls." Dispersion, bleeding, heat resistance, were spoken about.

Cleveland-Akron

Field Trip

R. L. Huber

On March 9th during the annual field trip, five plants of the Molded Fiber Glass Co., in Ashtabula, Ohio were visited. Various polyester applications in actual production were witnessed, including the White Motor Truck Cab., General Motors' Corvette body and a 17-foot one-piece outboard motor boat. About 150 attended this tour, which was followed later by dinner at the Swallows Restaurant.

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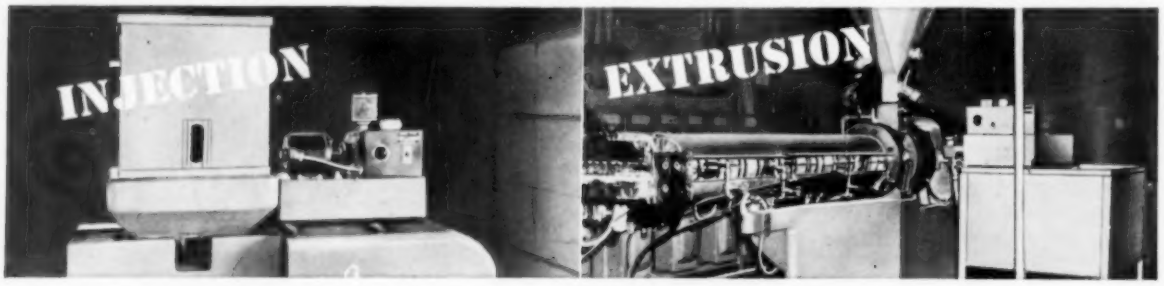

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Sheraton-Cadillac Hotel — Detroit, Mich.
June 30, 1959

Registration
9:00 A.M.

Morning Session
10:00 A.M.

"Evaluation of Plastic Tubing for Automotive Purposes"

Roy Deane—*The Spiratex Company* (speaker)

This paper deals with the properties of tubing made from various materials and their evaluation for automotive purposes.

10:30 A.M.

"Cost Advantages of Plastics in Replacement of Die Castings"

Dr. J. F. Woodman—*Tech. Asst. to Mgr. of Research & Dev., Rohm & Haas (Speaker)*

R. L. Gardner—*Sales Development, Molding Powders, Rohm & Haas (Co-author)*

D. A. Hurst—*Asst. Supervisor, Plastics Research & Dev. Labs., Rohm & Haas (Co-author)*

Individual case studies show that replacement of metal die castings by appropriate plastics can offer significant savings in cost. Plastic moldings can perform the essential functions of the metal parts and can either reproduce or improve their appearance. Specific plastics to be discussed include both conventional and high-impact acrylics and reinforced polyester premix.

11:15 A.M.

"Linear Polyethelene Molding of the 'Seat Side Shield' for the 1960 Ford"

Gordon Buehrig—*Ford Motor Co., Special Projects Dept., Advance Car Engineering—(Speaker)*

Thomas Risk—*Ford Motor Co., Special Projects Dept., Advance Car Engineering—(Co-author)*

This will be a case-history type discussion of the development of an actual plastic part to be used in the 1960 Ford automobile. Mr. Buehrig will be assisted by the following panel members who actively participated in the development of the application.

Joseph Rath—*J. B. Rath Co.*

Ralph Porter—*Phillips Chemical Co.*

Don Laramee—*Ford Motor Co., Brooklyn Molding Division*

Dale Pettry—*Ford Motor Co., Body Engineering Division*

Al Philips—*Ford Motor Co., Interior Styling Division*

Luncheon
12:30 P.M.

Luncheon Speakers:

Frederick C. Sutro, Jr., *SPE National President and* R. Kenneth Gossett, *SPE National Past President,* —"SPE Progress and Goals."

Dr. Robert E. Burk—*Associate Director, Research and Development Division, E. I. duPont de Nemours & Co., Inc.*

"The Dynamic Growth of Plastics in European Cars"

The European automotive industry is more dynamic than the U.S. in its use of plastics. This observation is based on actual contact and correspondence with essentially all of the European auto manufacturers since 1955. Among the points to be discussed is the use of larger moldings and the more rapid rate of growth as compared to the U.S. auto manufacturers. Through the cooperation of European firms, Dr. Burk will discuss their most current applications of plastics in the automotive industry.

Afternoon Session
2:15 P.M.

Moderator—Miller Sherwood, *Michigan Plastics Products*

"Blow Molding with High Density Polyethelene"

Thomas W. Mullen—*Sales Development Engineer, Celanese Corp. of America*

A study of the blow molding process, including types of equipment available, processing conditions as well as current automotive applications and potential markets. Additional papers and speakers to be announced prior to conference.

3:00 P.M.

Panel Discussion:

"The Difference in the Domestic and Foreign Outlook on the Use of Plastics in Automobiles"

Moderator: Harry McGowan—*Bakelite Co.*

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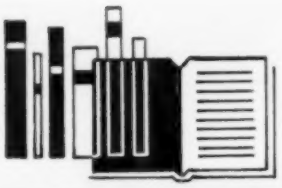

BOOK REVIEWS

GUM PLASTICS

M. S. Thompson, Reinhold Publishing Corp., 430 Park Ave., N.Y. 22, N.Y. 1958, 193 pages (5" x 7-1/2")

This is the ninth in a series of books on plastic applications. It is stated to be the first basic reference on "gum plastics" but gives virtually no references to the literature. The word gum used to refer to exudates from trees, including some that were water soluble. Some time ago it was extended to include other water swellable or soluble high molecular materials. Now it appears that the words "gum plastics" are being accepted as a name for inter- and intramolecular blends of rubber and plastics which give high impact strength values.

This book probably will fulfill its stated purpose—to show product designers, etc., why "rubber-modified (gum) plastic resins" have been used in commercial products. It does not serve the engineers and other scientists with a guide to or summary of the literature in the field.

Due to a minimum of numerical data and specific quantitative comparisons with other commercial materials in the first 53 pages, except for four general tables, the first part of the book can be summarized by a statement, "Gum plastics are worth trying in your commercial products."

Chapter 3 on "Basic Chemistry and Manufacture" gives very little chemical information. Chapter 4 on "Processing and Fabrication" reviews the modifications of standard production equipment and techniques for optimum processing of gum plastics. Chapter 5 on "Applications of Gum Plastics" gives a number of illustrations of the use of the unusual toughness of gum plastics in improving commercial products such as boats and wall coverings. The index is sufficient for the intended use of the book.

Robert B. Bennett
University of Florida

FLUOROCARBONS

Merritt A. Rudner. Reinhold Publishing Co., New York, 1958. 238 pp., $5.75.

This is the sixth of the Reinhold Plastics Application Series, and like the others is apparently intended to be a handy practical man's guide to the processing and use of polymeric materials, in this case the fluorocarbon resins. In this respect the book succeeds moderately well. It contains ten chapters which describe the general properties, the chemistry, processing techniques, the effects of fabrication variables on properties, discussions on electrical, mechanical and chemical applications, and the future of fluorocarbon resins. A good deal of practical information for the fabricator

and a limited amount for the designer and user of fluorocarbon resins is presented.

From the scientific and literary points of view, however, the book is very poor. It is poorly organized and repetitious. Its outstanding fault is its almost complete lack of critical appraisal. The author apparently had available a number of trade bulletins and journal articles which he used freely, but without any evidence of discrimination. For example, in several places polychlorotrifluoroethylene molding compositions from three suppliers are discussed, but at no time is any comparison of them made. Since there are no references given, except in the chapter on chemistry, the reader has no basis for judging the reliability of the statements made or the data given. Throughout the book there are an extraordinary number of errors of fact, usage, spelling and omission. Even the title is a misnomer. It should be "Fluorine-Containing Plastics" or at least "Fluorocarbon Plastics", but not "Fluorocarbons". It is asserted on page 26 that "Teflon 100X perfluorocarbon resins appear to have essentially the same electrical properties as the polymonochloroethylene resins and are not expected to have the flat frequency response and temperature stability of the normal "Teflon" tetrafluoroethylene resins." The author presumably meant polymonochloro**trifluoro**ethylene resins, but even so, the statement is misleading. Actually, except for a somewhat lower temperature ceiling, the electrical properties of "Teflon" 100X resemble those of "Teflon" TFE-fluorocarbon resin much more closely than they do the polychlorotrifluoroethylene resins. In the table on the next page a melt viscosity is quoted at a shear stress of 4.5 dynes/cm^2. This surely should be 4.5 x 10^5 dynes/cm^2. The one list of references and the bibliography contain many misspelled authors' names. This reviewer feels strongly that such a high concentration of errors is inexcusable on the part of both the author and the publisher.

The net conclusion is that this book will have very limited usefulness. It is not recommended as a general reference.

E. E. Lewis
E. I. DuPont DeNemours & Co.

WELDING OF PLASTICS

J. Alex Neumann and Frank J. Bockhoff. Reinhold Publishing Corp., New York, 1959. 279 pages. $7.25.

The authors have succeeded in compiling a wealth of information and presenting it in thirteen chapters covering all the practical welding techniques now in use as well as separate chapters on design, testing methods and special applications. Five appendices are included adding to the book's value especially for the design engineer.

Many photos, sketches and tables are used to supplement the presentation, the step-by-step illustrations should be valuable to anyone new to plastic welding. Other tables such as Table 9-I lists the practical, on-the-spot tests for identifying many common plastics.

As a text the book could be used in full or in parts. The Chapter on Layout, Forming and Machining includes good coverage of hot and cold bending techniques, vacuum forming principles and drilling, cutting and tapping.

As a reference book practical use could be made of it in design of parts particularly for new applications since the newer materials are discussed and the excellent chapter on special technique and applications

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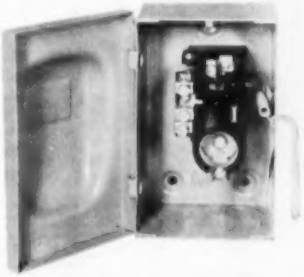

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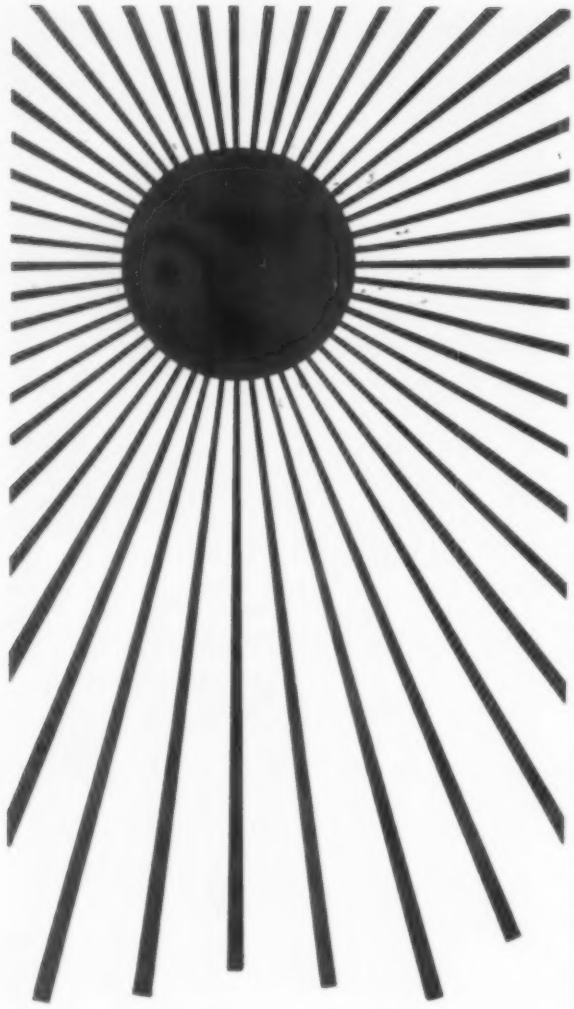

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discusses the many new possibilities of fabrication of such parts such as heat exchangers, filters and phase-separation equipment.

As a handbook some use may be had by the fabricator who is faced with short runs or custom made items. In place fabrication techniques are well presented, particularly for ducting and piping work.

The scope of the book is broad enough so that it can be recommended for any plastic library in view of the related fields covered. This is particularly true since many references are made to European practice, which in the field of welding seems to be out front due to the emphasis placed on this technique during the war. The authors have included references and, apparently obtained up-to-date information from sources overseas and have included these in a concise and well integrated manner throughout the book.

Frank C. Schutz
Welding Engineers, Inc.

BIG MOLECULES

Sir Harry Melville. The Macmillan Company, New York, 1958. 180 pp., $3.95.

Sir Harry Melville has written an altogether delightful and instructive little book. It reduces the complicated mass of theory and practice in polymer science and technology to a discussion easily read by anyone who has ever had a sound general course in chemistry. It is therefore not a reference book for the specialist, although it offers information to the technical man who may be curious about related fields of work.

There are six chapters: Making Big Molecules (synthesis); The Size of Big Molecules (molecular weight estimation); Fibres; Rubbers; Plastics (non-fiber applications of polymethylmethacrylate, polystyrene, polyethylene, polyvinyl chloride, polytetrafluoroethylene, and a little about adhesives); Polymers (cellulosic thickeners, polybasic acids, silicones and ion-exchange resins).

The book has a useful index, but lacks any bibliography or recommendation for further reading. The absence of an introduction leaves the reader dependent on the title for any idea of the purpose or limitations of the book. Several misprints mar an otherwise typographically fine production.

This book is to be particularly recommended to students, to junior staff men, and to non-technical people who sell, buy, or manage in the plastics field.

Charles H. Fuchsman
Ferro Chemical Corp.

ILLUSTRATED TECHNICAL DICTIONARY

Edited by Maxim Newmark. Philosophical Library, New York, 1958. 358 pages, $5.00.

This little book contains in its concise form a great deal of technical data, well selected and presented in alphabetical order. There are many illustrations, some of them supplied by the leading American industrialists and manufacturers. The last pages are devoted to geometrical shop data, American Standard abbreviations, units of weight and measures, temperature conversion tables and other information in table form. This inexpensive dictionary belongs on everyone's desk.

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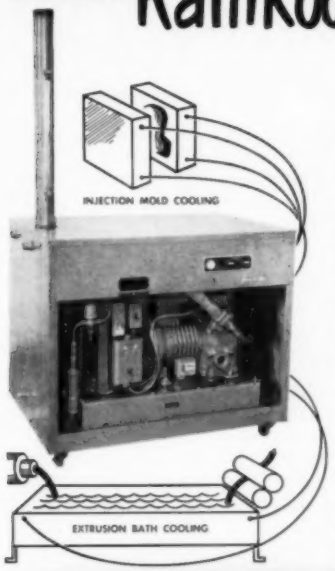

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Advertisers' Index

Aetna Standard, Division Blaw-Knox Company 354, 355
Allied Chemical Corp., National Aniline Division 342
Allied Chemical Corp., Plastics and Coal Chemicals Division 347
American Cyanamid Company, Plastics and Resins Division 361
Bee Chemical Co., Logo Division 348
Blaw-Knox Company, Aetna Standard Division 354, 355
Cadet Chemical Corp. 340
Carwin Company 441
Celanese Corporation of America, Chemical Division 352
Celanese Corporation of America, Plastics Division 339
Chemical Division, Celanese Corporation of America 352
Continental Carbon Company, Division of Wittco 360
Detroit Mold Engineering Company 353
Dow Chemical Company 365
Durez Plastics Division, Hooker Chemical Corporation 445
E. I. du Pont de Nemours & Co., Inc., Polychemicals Department 336
Eastman Chemicals Products, Inc. 349
Frank W. Egan & Company 358
Farrel-Birmingham Co., Inc., Watson-Stillman Press Division 350
General Dyestuff Company 431
Georgia Kaolin Company 427
Gering Products, Inc. 438
Harshaw Chemical Company 344
Hooker Chemical Corporation, Durez Plastics Division 445
Improved Machinery, Inc. 357
Injection Molders Supply Company 428
Interplastics Incorporated 437
Kentucky Color & Chemical 446
Logo Division, Bee Chemical Company 348
Manco Products, Inc. 438
Monsanto Chemical Company, Plastics Division 351
National Aniline Division, Allied Chemical Corp..... 342
National Distillers and Chemical Corp., U. S. Industrial Chemicals Co., Div. of 345, 346
National Rubber Machinery Company 364
Nixon Nitration Works 449
Phillips Chemical Company 450
Plastic Molders Supply Co., Inc. 436
Plastics & Coal Chemicals Division, Allied Chemical Corp. 347
Plastics Division, Celanese Corporation of America.... 339
Plastics & Resins Division, American Cyanamid Company 361
Polychemicals Department, E. I. du Pont de Nemours & Co., Inc. 336
Prodex Corporation 432
Rainville Company 447
Reichhold Chemicals, Inc. 359
Rohm & Haas Company 366
Sandoz, Inc. 337
Sterling, Inc. 444
Thoreson-McCosh, Inc. 442
Union Carbide Plastics Company, Division of Union Carbide Corporation 362, 363
U. S. Industrial Chemicals Co., Division of National Distillers and Chemical Corporation 345, 346
Van Dorn Iron Works Co. 338
Watson-Stillman Press Division, Farrel-Birmingham Co., Inc. 350
Westchester Plastics, Inc. 356
West Instrument Corporation 440
Wittco Division, Continental Carbon Company..... 360

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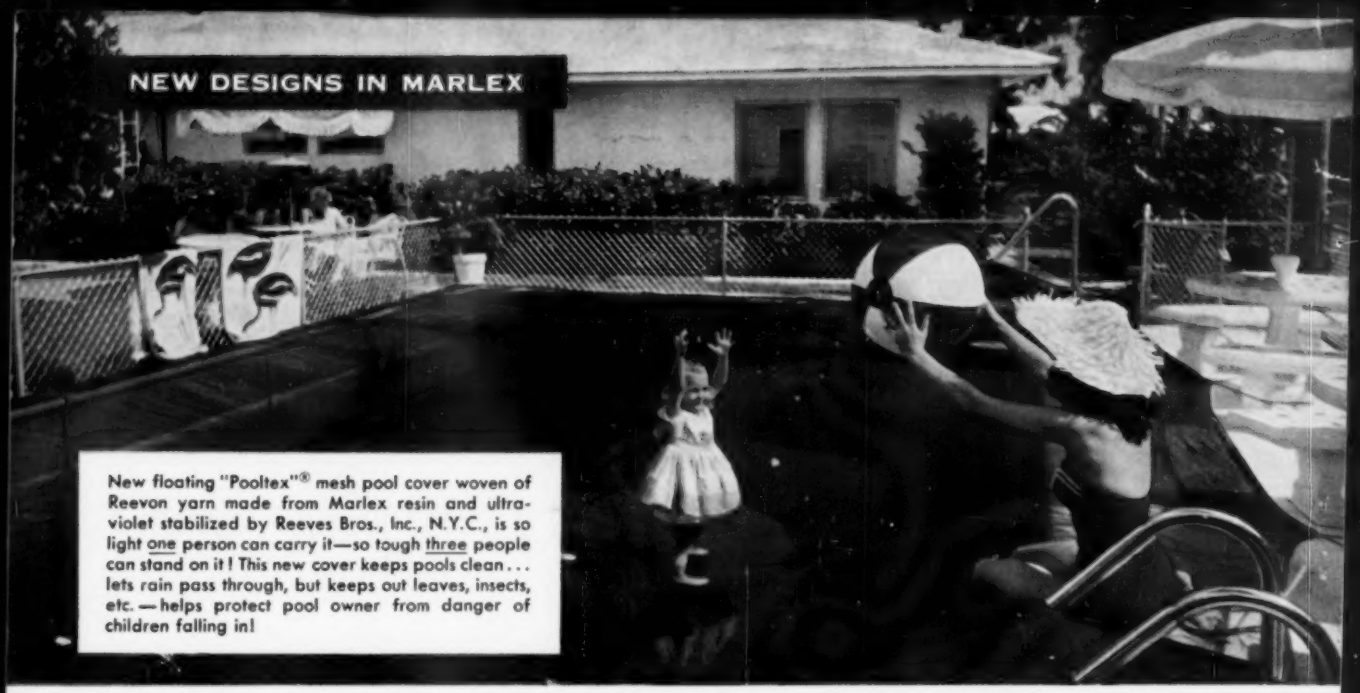

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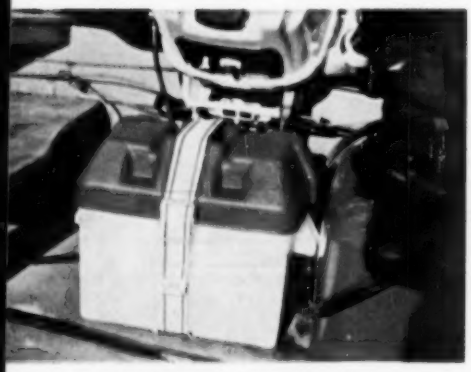

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